

МАКЕДОНСКО ГЕОГРАФСКО ДРУШТВО  
MACEDONIAN GEOGRAPHICAL SOCIETY



# ЗБОРНИК НА ТРУДОВИ

V КОНГРЕС НА ГЕОГРАФИТЕ ОД РЕПУБЛИКА МАКЕДОНИЈА

# PROCEEDINGS

V CONGRESS OF GEOGRAPHERS FROM REPUBLIC OF MACEDONIA

СКОПЈЕ / SKOPJE  
26 - 29 IX 2015



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#### **PUBLISHED BY**

Macedonian geographical society

ПОСЕБНО ИЗДАНИЕ

ISBN 978-608-65155-4-6

УДК: 91(497.7)(063)

91(497.7)(062)

# **ЗБОРНИК НА ТРУДОВИ ОД V КОНГРЕС НА ГЕОГРАФИТЕ НА РЕПУБЛИКА МАКЕДОНИЈА**

## **Издавач**

МАКЕДОНСКО ГЕОГРАФСКО ДРУШТВО

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SPECIAL EDITION

ISBN 978-608-65155-4-6

UDC: 91(497.7)(063)

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## SPELEOTHEMS IN THE CAVE SLATINSKI IZVOR

UDC:551.435.84(497.782)

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### Abstract

According to the environments in which speleothems are formed in the cave Slatinski Izvor, they belong to three groups: speleothems formed by flowing and dripping water, speleothems formed by capillary water and pool deposits. Three samples of speleothems were analyzed. In all samples the mineral calcite was detected. The chemical composition showed that CaO and SiO<sub>2</sub> were the dominantly represented, whereas Sr and B were the dominant trace elements in all rocky samples. Hydrochemical properties of water samples of three drips from the same cave were analyzed in the period December 2011 - October 2013, in the dry period of the year. Four methods (Piper diagram, Stiff diagram, Chadha diagram, and D'Amore diagram) were applied in order to determine the hydrochemical properties of the water samples. The results showed that all water samples had the same origin, dolomite rocks had the dominant impact of the drip water, HCO<sub>3</sub> and SO<sub>4</sub> were dominant dissolved species in the water, and there was no contaminants in the aquifer.

**Key words:** speleothems, cave Slatinski Izvor, mineralogical analysis, hydrochemical analysis

### INTRODUCTION

The water which passes through soil above the carbonate rocks absorbs high level of carbon dioxide, and it is able to dissolve a large amount of the underlying rocks. When water seeps into an air-filled cave, most of the dissolved carbon dioxide escapes into the cave atmosphere. As a result, the water is able to hold less calcium carbonate, and some of the dissolved load is deposited as speleothems (Palmer, 2007). Thus, speleothems are secondary mineral deposits formed by a physico-chemical reaction from a primary mineral within the cave environment (Hill & Forti, 1997). They are grouped according to the environments in which they form, and each type is identified with its basic shape. Dripping water provides access to water from the vadose zone (Kogovšek, 2010). Hydrochemical analyses of this water help to locate and quantify the mineralization of the water, provide information about the structure and dynamics of karst aquifer, help for understand the water-rock interactions (Gičevski & Hristovski, 2015) and aim at identifying the origin of water contamination.

Until now in Republic of Macedonia, the speleothems of the caves as well as the dripping water and its hydrochemical properties have not been subject to analysis. The main aim of this study was to classify the speleothems of the cave Slatinski Izvor and analyze them from the aspect of their mineralogical and hydrochemical characteristics.

### STUDY AREA

The Slatinski Izvor cave is the longest cave in the Republic of Macedonia. It is situated in the river valley of Slatinska Reka and it is a part of the protected area Monument of Nature "Slatinski Izvor". The cave belongs to the Pelagonian horst-anticlinorium tectonic unit, and it is built in pre-Cambrian dolomite marbles which are well karstified. The carbonate rocks are covered with Pliocene sediments (Dumurdzanov *et al.*, 1979) which are well permeable with intergranular porosity. The area above the cave is covered with mosaic termophyllous oak forest and dry grassland.

### METHODS

In order to identify the mineralogical and chemical composition of the speleothems from the cave, three samples of rock material were taken: the first one, stalagmite, at 800 m from the cave's entrance (SiK2), the second, stalactite, (SiK3) and the third one, stalactite, (SiK4) at 50 m distance from the cave's entrance. The macro and microelements properties of the rock material were analyzed with an Atomic emission spectroscopy with inductively coupled plasma (AES-ICP), LYBERTY 110 at the University "Goce Delčev" in Štip. Scanning electron microscopy (SEM) VEGA3 LMU was used for quantitative analysis of the rock samples. SEM analysis were made with SE



detector on 20 kV voltage. Vega TC software was used for SEM analysis. The following elements were analyzed: oxygen (O), calcium (Ca), magnesium (Mg), iron (Fe), silica (Si), potassium (K), sodium (Na), manganese (Mn), aluminium (Al), titanium (Ti), phosphorus (P), strontium (Sr), barium (Ba), zinc (Zn), chromium (Cr), lead (Pb), vanadium (V), molybdenum (Mo), copper (Cu), cobalt (Co), boron (B), nickel (Ni), cadmium (Cd), arsenic (As) and silver (Ag). The results for oxides of Ca, Mg, K, Na, Mn, P, Fe, Al, Ti and Si are presented in weight percentage, while the rest of the elements in  $\text{mg}\cdot\text{kg}^{-1}$ .

In order to identify the chemical characteristics of the drip waters, field measurements and laboratory analyses were carried out. The water samples were collected monthly, between December 2011 and November 2013, in the dry period of the year. A total of 7 water samples were collected from the Drip 1, 9 from the Drip 2 and Drip 3. Water temperature, pH and specific conductivity were measured *in-situ* at the time of sampling using the field instrument Lovibond CHECKIT Micro. Samples were collected manually in polyethylene bottles.

The hydrochemical properties were analyzed at the Institute of Biology, Faculty of Natural Sciences and Mathematics in Skopje, "Ss. Cyril and Methodius" University in Skopje. All water samples were filtered within 12 hours of collection and analyzed within 3-4 days. Sulphate was determined by photometric method of Dévai *et al.* (1973) and chlorides by Mohr's method (Škunca-Milovanović *et al.*, 1990). All of the major cations: sodium (Na), potassium (K), calcium (Ca), magnesium (Mg) as well as minor cations and trace elements: copper (Cu), cadmium (Cd), cobalt (Co), lead (Pb), manganese (Mn), zinc (Zn), iron (Fe) were analyzed by wet digestion followed by atomic absorption spectrometry on Agilent 55Z or graphite furnace Agilent 240Z (Allen 1989). Total phosphorus was determined in the same digested material by the method of Fiske & Subarow (1925). All of the values are presented in mass concentrations ( $\text{mg}\cdot\text{L}^{-1}$ ). Ca/Mg ratios were calculated based on values of respective ions expressed in  $\text{meq}\cdot\text{L}^{-1}$ .

For the interpretation of the chemical analyses, four graphical methods were used. The data were plotted on a trilinear Piper diagram (Piper, 1944). The major cations and anions are plotted in milligram per liter ( $\text{mg}\cdot\text{L}^{-1}$ ), in each triangle, then the plotting from triangular fields was extended further into the central diamond field. The Piper diagram was used to identify the water composition type and rock types of the aquifer. In the Stiff diagram (Stiff, 1951) cations are plotted on the left side of the zero axis, and anions are plotted on the right side, both in milliequivalents per liter ( $\text{meq}\cdot\text{L}^{-1}$ ). Each different pattern represents a different type of water. In the Chadha diagram (Chadha, 1999) the difference in milliequivalent percentage between alkaline earth metals (Ca+Mg) and alkali metals (Na+K), expressed as percentage reacting values, is plotted on the X-axis, and the difference in milliequivalent percentage between weak acidic anions (carbonate + bicarbonate) and strong acidic anions (chloride + sulphate) is plotted on the Y-axis. The milliequivalent percentage differences between alkaline earths and alkali metals, and between weak acidic anions and strong acidic anions may plot in one of the four possible sub-fields of the proposed diagram. The square or rectangular field describes the overall character of the water. Using basic cations and anions D'Amore *et al.* (1983) determined six new parameters for distinguishing water groups based on the geological features of the main reservoir crossed by each water sample. Hydrochemical parameters are marked by letters from A to F. Parameters define the ratio between dissolved species in  $\text{meq}\cdot\text{L}^{-1}$ , and range from +100 to -100  $\text{meq}\cdot\text{L}^{-1}$ .

The saturation indexes (SI) of minerals (anhydrite, aragonite, calcite, dolomite, gypsum and halite) available in the aquifer were calculated using WATEQ4F computer program (Plummer *et al.*, 1976). If the water is exactly saturated with the dissolving mineral, saturation index equals to zero. Positive values of saturation index indicate saturation, and negative ones indicate undersaturation.

## RESULTS AND DISCUSSION

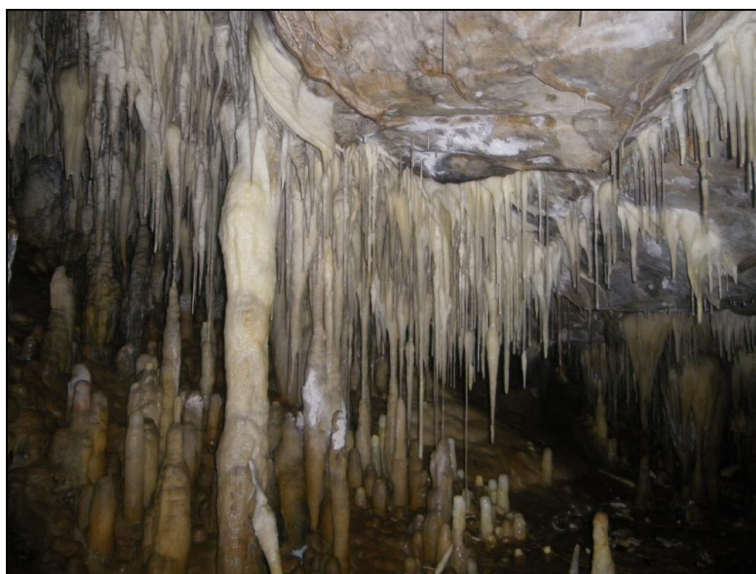
### Speleothems classification

The speleothems are arranged in groups according to the nature of the water that on deposits them (Palmer, 2007). They belong to three groups: speleothems formed by flowing and dripping water, speleothems formed by capillary water and pool deposits.

The terminology of speleothems is according to Hill & Forti (1997). The most numerous are formed by flowing and dripping water, represented by flowstones (fig. 1), stalactites (figs. 1, 2), soda straws, draperies, stalagmites (fig. 2), columns (fig. 2) and conulites. The group of speleothems formed by capillary water is represented by helictites. These speleothems are found throughout the cave. They are in white, yellow and brown color. Shelfstone (especially crescent shelfstone) (fig. 3), subaqueous coralloids, bulbous stalactites (war club stalactites) (fig. 4), raft cones and folia are most impressive pool deposits in the cave. Most of them are dark brown. They are located between 1.5 and 3 km from the cave's entrance. War club stalactites have ~10 cm in diameter and are only noticed in this cave in the Republic of Macedonia.



**Figure 1:** Flowstones and dripstones



**Figure 2:** Stalactites, stalagmites and column



**Figure 3:** Crescent shelfstone



**Figure 4:** Bulbous stalactites (war-club stalactites)

### Mineralogical characteristics

SEM analysis showed that the first rocky sample (SiK2) is composed of oxygen (55.86 %) and Ca (44.14 %), the second sample (SiK3) is composed of oxygen (69.44 %) and Ca (30.56 %), whereas the third sample (SiK4) is composed of oxygen (59.65 %) and Ca (40.35 %). The chemical composition of the rock samples (Tab. 1) showed that CaO and SiO<sub>2</sub> are the dominantly represented. Sr and B are the dominant trace elements in all rock samples.

**Table 1:** Chemical composition and trace elements of the rock samples from the cave Slatinski Izvor (SiK2- stalagmite, SiK3, SiK4-stalactite).

	SiK2	SiK3	SiK4
SiO <sub>2</sub> (%)	8.12	8.08	1.75
Al <sub>2</sub> O <sub>3</sub> (%)	0.02	0.01	0.01
CaO (%)	46.1	47.5	54.4
MgO (%)	0.77	0.16	0.17
Na <sub>2</sub> O (%)	0.01	0.02	0.02
K <sub>2</sub> O (%)	0.01	0.01	0.01
FeO (%)	0.01	0.00	0.01
MnO (%)	0.00	0.00	0.00
P <sub>2</sub> O <sub>5</sub> (%)	0.01	0.01	0.02
TiO <sub>2</sub> (%)	0.00030	0.00030	0.00030
Ashing loss (%)	44.7	43.9	43.4
Total	99.77	99.74	99.80
Sr (mg/kg)	72.38	241.75	76.40
Ba (mg/kg)	8.69	24.53	26.77
Zn (mg/kg)	<2	<2	<2
Cr (mg/kg)	<2	<2	<2
Pb (mg/kg)	<2	2.15	2.34
V (mg/kg)	1.26	5.31	1.50
Mo (mg/kg)	1.17	3.24	2.59
Cu (mg/kg)	2.38	<2	<2
Co (mg/kg)	<2	<2	<2
B (mg/kg)	2.97	0.93	1.04
Ni (mg/kg)	<2	<2	<2
Cd (mg/kg)	<1	<1	<1
As (mg/kg)	1.56	7.53	5.53
Ag (mg/kg)	0.19	0.57	0.33

### General hydrochemical composition of the drip waters

The physical and chemical characteristics of the waters are presented in Table 2. Regarding the temperature all drips in the cave showed very constant values. Average temperature of Drip 1 was 10.57°C, of Drip 2 was 10.65°C, and of Drip 3 was 10.6°C, all oscillating in an interval from 10 to 11°C. All water samples showed alkaline reaction. The pH values of Drip 1 were oscillating in an interval from 8.0 to 8.2, and for Drip 2 and Drip 3 the pH values were oscillating between 8.0 and 8.4. The mean values of electrical conductivity were 400  $\mu\text{S}\cdot\text{cm}^{-1}$  for Drip 1, 377  $\mu\text{S}\cdot\text{cm}^{-1}$  for Drip 2 and 388  $\mu\text{S}\cdot\text{cm}^{-1}$  for Drip 3. All water samples had *hard water*.

**Table 2:** Hydrochemical properties of the drip waters from the cave Slatinski Izvor, for the dry period between December 2011-October 2013. CV-coefficient of variation, TDS-total dissolved solids, n-number of water samples.

	Drip 1 (n=7)	Drip 2 (n=9)	Drip 3 (n=9)
<i>T</i> (°C)			
Range	10-12	10-12	10-12
Mean	10.71	11.18	10.8
CV	0.06	0.08	0.07
<i>pH</i>			
Range	8.0-8.2	8.0-8.4	8.0-8.4
Mean	8.07	8.13	8.18
CV	0.01	0.01	0.02
<i>EC</i> ( $\mu\text{S}\cdot\text{cm}^{-1}$ )			
Range	400	350-400	350-400
Mean	400	377	388
CV	0.00	0.06	0.05
<i>TDS</i> ( $\text{mg}\cdot\text{L}^{-1}$ )			
Range	256	224-256	224-256
Mean	256	241.77	248.88
CV	0.00	0.06	0.05
<i>Ca</i> <sup>2+</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )			
Range	10.14-23.53	7.63-48.95	14.52-38.66
Mean	16.32	18.97	21.48
CV	0.28	0.64	0.32
<i>Mg</i> <sup>2+</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )			
Range	11.36-43.06	9.89-46.28	12.25-47.65
Mean	21.41	25.27	24.71
CV	0.28	0.56	0.51
<i>Cl</i> ( $\text{mg}\cdot\text{L}^{-1}$ )			
Range	8.4-13.2	7.3-11.6	6.4-10.8
Mean	10.31	9.34	8.48
CV	0.17	0.16	0.18
<i>Na</i> <sup>+</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )			
Range	0.42-1.10	0.58-3.11	0.84-1.36
Mean	0.94	1.32	1.03
CV	0.23	0.55	0.16
<i>K</i> <sup>+</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )			
Range	0.12-0.36	0.13-1.03	0.19-0.43
Mean	0.28	0.31	0.30
CV	0.31	0.84	0.26
<i>SO</i> <sub>4</sub> <sup>2-</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )			
Range	27.79-91.64	25.90-86.80	16.58-82.69
Mean	51.80	42.84	34.86
CV	0.46	0.45	0.52
<i>HCO</i> <sub>3</sub> <sup>-</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )			
Range	61.0-67.1	67.1-109.8	109.8-140.3
Mean	62.74	93.53	117.93
CV	0.04	0.17	0.09
<i>NO</i> <sub>3</sub> <sup>-</sup> ( $\text{mg}\cdot\text{L}^{-1}$ )			
Range	0.00-3.42	0.00-1.13	0.00-2.13

Mean	1.82	0.45	0.50
CV	0.58	0.92	1.28
$NO_2^-$ ( $mg \cdot L^{-1}$ )			
Range	0.00-0.22	0.00-0.24	0.00-0.06
Mean	0.03	0.03	0.01
CV	2.26	1.99	1.53
$NH_4^+$ ( $mg \cdot L^{-1}$ )			
Range	0.16-0.73	0.09-0.84	0.10-0.63
Mean	0.43	0.39	0.35
CV	0.49	0.62	0.50

The major ions in all water samples were dominantly  $Mg^{2+} > Ca^{2+} > Na^+$  for the cations and  $HCO_3^- > SO_4^{2-} > Cl^-$  for the anions.  $HCO_3^-$  and  $SO_4^{2-}$  were dominant dissolved species in the water (tab. 2).

The average hardness of the water samples of Drip 1, Drip 2 and Drip 3 were  $128.11 \text{ mg} \cdot L^{-1}$ ,  $150.46 \text{ mg} \cdot L^{-1}$  and  $154.68 \text{ mg} \cdot L^{-1}$ , respectively. According to Sawyer and McCarty's (1967) classification the water samples fall under *moderately hard* ( $75-150 \text{ mg} \cdot L^{-1}$ ) to *hard classes* ( $150-300 \text{ mg} \cdot L^{-1}$ ).

The values of Ca/Mg ratio of the Drip 1, Drip 2 and Drip 3 were 0.60, 0.59 and 0.63, respectively. These values show that the dolomite rocks have the dominant impact of the drip water.

All water samples showed the low impact of the contaminants through the vadose zone of karst. The average values of the water contaminants in the Drip 1 were as follows:  $NO_3^- = 1.82 \text{ mg} \cdot L^{-1}$ ,  $NO_2^- = 0.03 \text{ mg} \cdot L^{-1}$ ,  $NH_4^+ = 0.43 \text{ mg} \cdot L^{-1}$ , and  $PO_4^{3-} = 0.01 \text{ mg} \cdot L^{-1}$ . The mean values of the mentioned parameters for the Drip 2 were  $0.45 \text{ mg} \cdot L^{-1}$ ,  $0.03 \text{ mg} \cdot L^{-1}$ ,  $0.39 \text{ mg} \cdot L^{-1}$ ,  $0.02 \text{ mg} \cdot L^{-1}$ , and for the Drip 3 were  $0.50 \text{ mg} \cdot L^{-1}$ ,  $0.01 \text{ mg} \cdot L^{-1}$ ,  $0.35 \text{ mg} \cdot L^{-1}$ ,  $0.00 \text{ mg} \cdot L^{-1}$ , respectively.

The concentrations of trace elements (Cu, Cd, Co, Pb, Mn, Zn, Fe, P) in the water were low (Tab. 3). The highest concentration had Cu which may be derived from dissolution of carbonates.

**Table 3:** Trace elements in the water samples of the Drips 1, 2, 3 from the cave Slatinski Izvor.

	concentration range ( $\mu\text{g} \cdot L^{-1}$ )				concentration range ( $\text{mg} \cdot L^{-1}$ )		
	Drip 1	Drip 2	Drip 3		Drip 1	Drip 2	Drip 3
Cu	0.934-3.875	1.130-4.438	1.103-3.938	Mn	0.000-0.009	0.001-0.035	0.001-0.003
Cd	0.000-0.089	nd-0.051	nd-0.291	Zn	0.003-0.008	0.004-0.021	0.004-0.011
Co	nd-0.124	nd-0.865	nd-0.051	Fe	0.008-0.376	0.018-1.613	0.017-0.067
Pb	nd-0.099	nd-0.022	nd-0.059	P	0.000-0.082	0.000-0.122	0.002-0.042

### Saturation indices

Saturation indices of the water samples are given in Table 4. All water samples of the Drip 1 were undersaturated with respect to anhydrite, aragonite, calcite, dolomite, gypsum and halite. All water samples of the Drip 2 were undersaturated with respect to anhydrite, aragonite, dolomite, gypsum and halite. Undersaturation occurred in all water samples with respect to calcite, except one sample (December-2011) was slightly saturated with respect to calcite. All water samples of the Drip 3 were undersaturated with respect to anhydrite, aragonite, gypsum and halite. Generally, undersaturation occurred in six of analyzed water samples with respect to calcite, whereas three samples (August-2012, July-2013, October-2013) were slightly saturated with respect to calcite. Five water samples (December-2011, July-2012, November-2012, August-2013, September-2013) were generally undersaturated with respect to dolomite, and four water samples (August-2012, October-2012, July-2013, October-2013) were slightly saturated with respect to dolomite.

**Table 4:** Saturation indices of the water samples of the drip waters in the Slatinski Izvor cave.

Date of sampling	Anhydrite	Aragonite	Calcite	Dolomite	Gypsum	Halite
Sampling point: Drip 1						
03.12.2011	-2.651	-0.737	-0.582	-1.085	-2.531	-9.877
21.07.2012	-2.459	-0.979	-0.825	-1.102	-2.350	-9.657
12.08.2012	-2.373	-0.898	-0.744	-1.035	-2.264	-9.562
02.10.2012	-2.560	-0.622	-0.467	-0.594	-2.441	-9.504
28.07.2013	-2.689	-0.756	-0.603	-1.223	-2.591	-9.377
10.08.2013	-2.374	-0.583	-0.429	-0.961	-2.265	-9.362
20.10.2013	-2.565	-0.498	-0.343	-0.848	-2.446	-9.556

Sampling point: Drip 2						
03.12.2011	-2.032	-0.101	0.54	-0.179	-1.913	-9.172
21.07.2012	-2.293	-0.438	-0.284	-0.037	-2.196	-9.561
12.08.2012	-2.522	-0.705	-0.551	-0.455	-2.424	-9.310
02.10.2012	-2.843	-0.825	-0.670	-0.638	-2.729	-9.577
23.11.2012	-2.628	-0.331	-0.176	-0.063	-2.511	-9.601
28.07.2013	-2.746	-0.284	-0.131	-0.236	-2.648	-9.469
10.08.2013	-2.918	-0.824	-0.670	-1.092	-2.820	-9.684
15.09.2013	-2.561	-0.670	-0.516	-1.076	-2.464	-9.453
20.10.2013	-2.539	-0.210	-0.055	-0.270	-2.420	-9.557
Sampling point: Drip 3						
03.12.2011	-2.839	-0.372	-0.216	-0.226	-2.720	-9.740
21.07.2012	-2.475	-0.367	-0.213	-0.118	-2.367	-9.631
12.08.2012	-2.013	-0.115	0.039	0.264	-1.905	-9.528
02.10.2012	-2.816	-0.214	-0.059	0.303	-2.697	-9.575
23.11.2012	-2.840	-0.318	-0.163	-0.066	-2.729	-9.560
28.07.2013	-2.652	-0.059	0.095	0.132	-2.543	-9.543
10.08.2013	-2.523	-0.243	-0.090	-0.260	-2.425	-9.474
15.09.2013	-2.498	-0.214	-0.060	-0.300	-2.400	-9.579
20.10.2013	-2.716	-0.122	0.033	0.005	-2.597	-9.688

### Grapho- analytical methods

Cation and anion concentrations are presented on Piper diagram (fig. 5). The chemical composition of the dripping water showed that water has temporary hardness, alkaline earths ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ) exceed alkalis ( $\text{Na}^+ + \text{K}^+$ ), weak acidic anions ( $\text{CO}_3^{2-} + \text{HCO}_3^-$ ) exceed ( $\text{Na}^+ + \text{K}^+$ ) and water is characterized by Mg- $\text{HCO}_3$  type. Only two water samples of the Drip 1 and one water sample of the Drip 2 showed permanent hardness, and belong to Ca- $\text{SO}_4$  type of water.

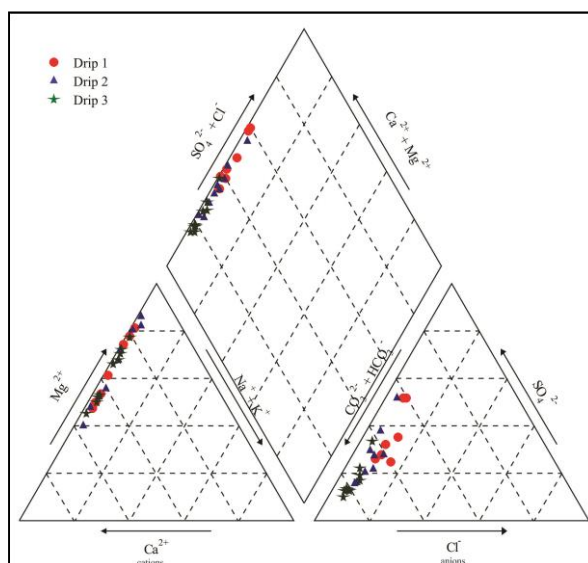
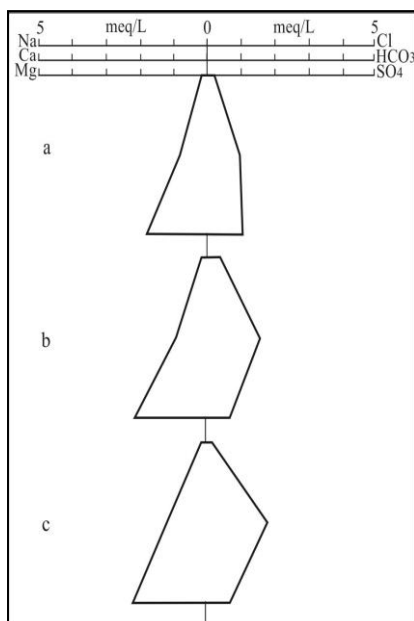


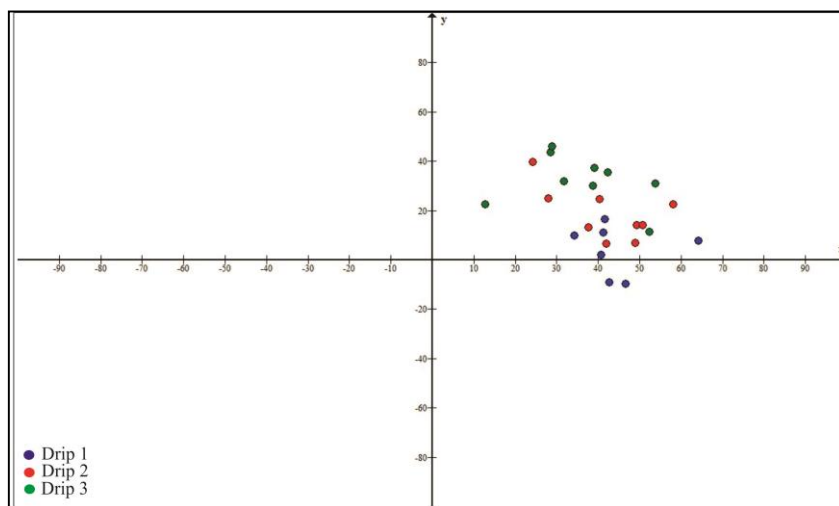
Figure 5: Piper diagram of the drip water from the cave Slatinski Izvor.

Stiff diagram (fig. 6) shows that carbonates, especially Mg content had certain influence on trickles.



**Figure 6:** Stiff diagram of the drips in the cave Slatinski Izvor (a-Drip 1, b-Drip 2, c-Drip 3).

Five water samples of the Drip 1 fall in the 5th sub-field of Chadha diagram (fig. 7). Alkaline earths ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ) and weak acidic anions ( $\text{CO}_3^{2-} + \text{HCO}_3^-$ ) exceed both alkali metals ( $\text{Na}^+ + \text{K}^+$ ) and strong acidic anions ( $\text{Cl}^- + \text{SO}_4^{2-}$ ). Two water samples, taken in July 2012 and in August 2012, fall in the 6th sub-field. This indicates that alkaline earths ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ) exceed alkali metals ( $\text{Na}^+ + \text{K}^+$ ) and strong acidic anions ( $\text{Cl}^- + \text{SO}_4^{2-}$ ) exceed weak acidic anions ( $\text{CO}_3^{2-} + \text{HCO}_3^-$ ). These two water samples had permanent hardness, and represent  $\text{Ca}^{2+}$ - $\text{Mg}^{2+}$  dominant  $\text{Cl}^-$  type waters. All water samples of Drips 2 and 3 fall in the 5th sub-field of Chadha diagram (fig. 7). This indicates that alkaline earths ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ) and weak acidic anions ( $\text{CO}_3^{2-} + \text{HCO}_3^-$ ) exceed both alkali metals ( $\text{Na}^+ + \text{K}^+$ ) and strong acidic anions ( $\text{Cl}^- + \text{SO}_4^{2-}$ ), respectively. Such waters have temporary hardness. The position of data points in the diagram represent  $\text{HCO}_3^-$  - dominant  $\text{Ca}^{2+}$ - $\text{Mg}^{2+}$  type waters.



**Figure 7:** Chadha diagram of the drip water from the cave Slatinski Izvor.

The water samples of the drips in the cave belong to D'Amore  $\alpha$  type which are represented by  $\text{CaSO}_4$  type water. All drip waters had nearly identical pattern on D'Amore diagram (fig. 8). The Drips 2 and 3 had positive values of the A parameter which emphasizes the influence of the carbonates on the water. The same parameter of the Drip 1 points out that the impact of the evaporate rocks is low. The positive values of the B parameter point out water movement through rocks that contain sulphates. The values of the C parameter exclude the essential influence of flysch and clayey sediments in the formation of the water. The negative values of the D parameter and positive values of the E parameter point out water circulation through carbonate rocks. The high values of the F parameter emphasize that calcium content is significantly higher in relation to sodium and potassium.

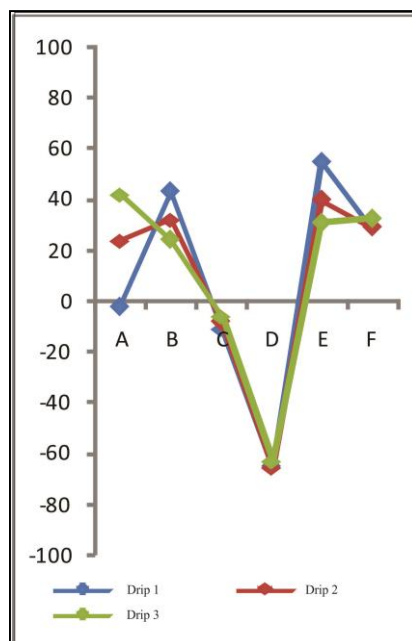


Figure 8: D'Amore rectangular diagram of the drips in the cave Slatinski Izvor.

## CONCLUSION

This study is a results of a continuous research in the cave Slatinski Izvor, aiming to classify speleothems and to determine their mineralogical and hydrochemical properties.

The speleothems of the cave Slatinski Izvor belong to three groups: speleothems formed by flowing and dripping water (flowstones, stalactites, draperies, stalagmites, columns, conulites), speleothems formed by capillary water (helictites) and pool deposits (shelfstone, subaqueous coralloids, bulbous stalactites, raft cones, folia).

The chemical composition of three rock samples showed that CaO and SiO<sub>2</sub> are dominantly represented, whereas Sr and B are the dominant trace elements in all rock samples.

During the dry period of the year, hydrochemical analysis of dripping water showed that HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were dominant dissolved species in the water. The values of Ca/Mg ratio show that the dolomite rocks have the dominant impact on the drip water. All water samples showed low impact of the contaminants through the vadose zone of karst. The concentrations of Cu, Cd, Co, Pb, Mn, Zn, Fe, P in the water were low.

All drip waters had nearly identical patterns on Piper, Stiff, Charha and D'Amore diagrams.

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## УКРАСИ ВО ПЕШТЕРАТА СЛАТИНСКИ ИЗВОР

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### Абстракт

Според условите во кои се формирани, украсите во пештерата Слатински Извор припаѓаат на три групи: украси формирани од вода што тече и вода прокапница, украси формирани од капиларна вода и басенски депозити. Три пештерски украси беа анализирани, при што минералот калцит беше евидентиран кај сите. Кај сите примероци на карпи, хемискиот состав покажа дека CaO и SiO<sub>2</sub> се доминантно застапени, додека Sr и B се доминантни од елементи во траги.

Во периодот декември 2011 - октомври 2013, во сувиот период од годината, беа анализирани хидрохемиските карактеристики на водата прокапница од три украси. Четири методи (Piper дијаграм, Stiff дијаграм, Chadha дијаграм и D'Amore дијаграм) беа употребени за определување на хидрохемиските одлики на примероците вода. Резултатите покажаа дека сите примероци на вода имаат исто потекло, карпата доломит има доминантно влијание врз водата прокапница, HCO<sub>3</sub><sup>-</sup> и SO<sub>4</sub><sup>2-</sup> се доминантно растворени во водата и во карсниот издан нема загадувачи.

**Клучни зборови:** пештерски украси, пештера Слатински Извор, минералошки анализи, хидрохемиски анализи