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Редактори:
Петър СТЕФАНОВ
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Диляна СТЕФАНОВА
Димитрина МИХОВА

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CHEMICAL AND TEXTURAL COMPOSITION OF THE KRKA RIVER TUFA DEPOSITS FROM THE DINARIC KARST REGION OF CROATIA

Medunić G.[1], Juranović Cindrić I.[2], Pivčević N.[1], Kampić Š.[1], Prohić E.[1], Goreta G.[3], Čobić A.[1]

[1] Institute of Mineralogy and Petrology, Faculty of Science, University of Zagreb, Horvatovac 95, HR-10000 Zagreb, Croatia; E-mail: gpavlovi@inet.hr
[2] Laboratory of Analytical Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-10000 Zagreb, Croatia;
[3] Krka National Park, National Institute, Trg Ivana Pavla II br. 5, HR-22000 Šibenik, Croatia.

Abstract. Tufa deposits, carbonates precipitated by freshwater organic and inorganic processes, occur abundantly in the Krka National Park situated inside the Dinaric Karst region of Croatia, at past and present sites of waterfalls. Chemical, petrographic and statistical analyses were carried out on six tufa samples to relate their textural constituents and trace element composition to the geochemical processes operating within this diverse environment. Trace metal concentrations in carbonate phase were analysed by the ICP-AES method, after a single extraction with 1M Na-acetate. The insoluble residue (I.R.) ranging from 2.20 to 21.10% (median 3.70%) could have resulted from the karstic weathering processes, influencing the tufa samples chemical composition. Generally, increased Fe, Mn, and I.R. levels are accompanied by decreased Sr and Mg levels, and vice versa.

Key words: *tufa, sequential extraction, mossy encrustation, traces metal correlation, re-crystallisation, Krka river*

Introduction

The Krka National Park is situated near the city of Šibenik on the Adriatic Coast of southern Croatia. It was proclaimed in 1985, although several sections of the Krka River were already protected as early as 1948. Geographically, this region is called Central Dalmatia where the Krka River, which is 72.5 km long, flows into the Adriatic Sea (Fig. 1).

Geotectonically, the area belongs to the unit known as the External Dinarides, representing a stable carbonate platform without terrigenous influence (the Adriatic carbonate platform, sensu Vlahović et al., 2005) that existed from the latest Triassic and punctuated by episodes of drowning or emersions, persisted into the Eocene. Karst topography and residue of variable thickness from the weathering of strata typifies this area. Since glacial times, the Krka River canyon has been incised in the Upper Cretaceous limestones and dolomites and Paleogene limestone conglomerates and breccias of the Promina Deposits (Mamužić, 1975). The Krka River with its series of spectacular waterfalls and cascades (i.e. carbonate barriers), the lakes behind them and the estuary, represents a well-known karst phenomenon. The estuary covers the part of an ancient river valley between the last active tufa barrier (the Skradinski Buk waterfalls, height 46 m), through the Prokljan Lake to the Šibenik Channel, with total length of 23.5 km. The most prominent features of this specific biotop are rapid current and sprinkling water abounding in dissolved bicarbonates, together with the micro- and macro-biological communities which flourish on the tufa barriers, contributing to the build-up of dams (Matoničkin & Pavletić, 1961). The constructive role of aquatic mosses, eukaryotic microorganisms and calcifying cyanobacteria has been extensively studied for a number of years (Golubić, 1969; Pedley, 1990, 1992; Golubić et al., 2008).

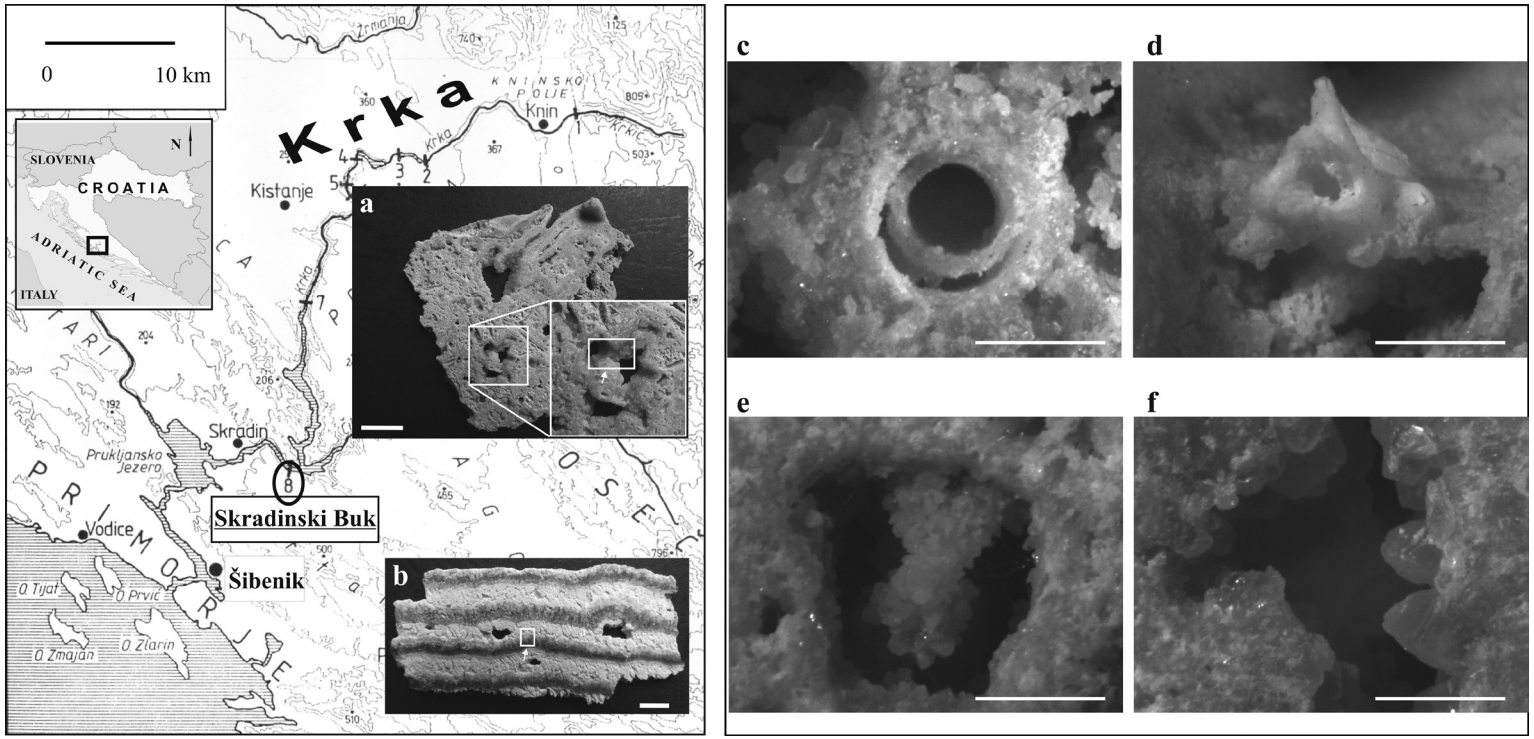

***Fig. 1**. Geographical location of the study area (in frame within the insert); two photographs (a – specimen K2, and b – specimen K3) of the slices show different morphologies of tufas, whereas four photographs (c – f) under the stereo microscope represent a few details of the specimen K2 Scale in Figs. a-f is 1 mm long.*

The locality has been studied using mainly isotope methods (Horvatinčić et al., 2000; Lojen et al., 2004), whereas elemental analyses (Fe, Mn, Sr, Mg, Pb, etc.) were carried out on composite samples (i.e. carbonate phase together with the insoluble residue) by means of XRF (Frančišković-Bilinski et al., 2004) and ICP-AES (Cukrov & Lojen, 2010); there have been no petrographic studies. Due to the paucity of research integrating geochemical data from the Krka River tufa deposits with their textural and mineral composition, this study has been initiated to characterise them by chemical, petrographical and mineralogical analyses. Hereby, this paper presents data on geochemical and petrographic features of the Krka River tufa deposits.

Materials and methods

Tufa samples were collected at the location Skradinski Buk waterfall which is 49 km downstream of the spring, at an altitude of 20 m above sea level. In fact, the locality consists of 17 cascades with the greatest volume of water, up to 100 m wide and 400 m of total length, whereas the total height is 46 m (Friganović, 1984). A total of six samples were taken either from the river bank (dry barrier) or from the crest of the cascade in contact with the water (Tab.1).

Table 1. *Macroscopic description of the tufa samples*

	Morphological type	Macroscopic features
K1	Mossy deposit	Hard; highly porous; plenty of encrusted organic material and clastic organic remains – heterogenous fabric; lace-like in slices
K2	Mossy deposit	Slightly harder than K1; the rest attributes as for K1
K3	Algally laminated crust	Very hard, dense rock; perfect light and dark laminations (cake-like in slices)
K4	'Algally laminated crust'	Barely visible, scarce laminations inside of rather crumbly (soft) fabric; medium plant cover on the surface
K5	'Algally laminated crust'	Comparing to K4, better laminated fabric (stromatolitic fashion), still friable; barren plant cover on the surface
K6	Difficult to classify (algally mediated?)	No lamination at all; very friable, homogenous, clayey fabric; rich (green) mossy cover on the surface

Thin sections were made of four samples (K1, K2, K3, and K4), where prior to slabbing the samples K1 and K4 were impregnated under vacuum with epoxy resin due to their crumbly fabric. The micro-morphological characteristics were analysed by polarised light microscopy. Stereo microscopic photographs were taken using Oly U-CMAD3 and QuickPHOTO CAMERA 2.3 software. The tufa phase composition was determined by X-ray diffraction analysis, carried out on Philips PW 3040/60 X'Pert PRO powder diffractometer (PANalytical) using CuKα radiation (λ = 1.54055 Å) at 40 kV and 40 mA. The organic matter content was determined by loss on ignition at 550oC for 2.5 hours. For the purpose of chemical analyses, the sample material was disaggregated, homogenised and ground in an agate mortar. Trace element concentrations in carbonate phase were measured after a single extraction with 1M Na-acetate (Tessier et al., 1979; Cook, 1992). The procedure was as follows: a reprsentative 10 g was continually mixed with 325 ml 1M Na-acetate ($NaC_2H_3O_2$) for 6 hours. Drops of acetic acid ($HC_2H_3O_2$), buffering pH value at 5, were carefully added since lower pH values may result in dissolution of non-carbonate components (Cook, 1992). Following this procedure, the extract solutions were filtered whereas the insoluble residues were dried and weighted. Trace element concentrations were analysed by a Prodigy High Dispersive ICP-AES spectrometer

(Teledyne Leeman, Hudson, NH, USA), operating in a simultaneous mode, and equipped with a glass concentric nebuliser. All measurements were run in triplicate. Data processing was performed with the STATISTICA Version 7 software.

Results

Calcite was found to be the predominant mineral in tufa samples, whereas quartz, 10 Å phyllosilicate (illite and/or mica), chlorite, K-feldspar, amphibole, and smectite were detected in the insoluble residue. The results of chemical analyses together with the basic statistical parameters of the measured variables are listed in Table 2.

Table 2. *Results of geochemical analyses: trace metal levels (µg/g) in carbonate phase; O.M. (organic matter) and I.R. (insoluble residue) expressed in %wt on the basis of the whole rock*

Samples	Fe	Mn	Sr	Mg	Zn	Pb	Cd	Cr	O.M.	I.R.
K1	11.60	20.00	82.4	525.0	2.50	3.95	0.95	2.30	2.0	3.7
K2	0.00	5.35	103.0	689.0	2.75	1.65	1.15	2.55	0.5	3.1
K3	3.10	11.40	144.0	561.0	5.65	4.75	1.05	5.20	0.8	3.7
K4	3.65	17.50	102.0	614.0	2.35	2.00	1.20	2.20	1.6	2.2
K5	8.30	27.30	88.2	604.0	4.30	2.85	0.90	4.15	1.2	3.9
K6	21.75	53.80	85.3	529.0	21.50	1.85	1.05	20.10	3.5	21.1
Basic statistical parameters (SD – standard deviation)										
Median	5.98	18.75	95.10	582.50	3.52	2.42	1.05	3.35	1.40	3.70
Min	0.00	5.35	82.40	525.00	2.35	1.65	0.90	2.20	0.50	2.20
Max	21.75	53.80	144.00	689.00	21.50	4.75	1.20	20.10	3.50	21.10
SD	7.86	17.04	22.85	62.14	7.45	1.26	0.11	6.97	1.08	7.29

The precission of the chemical analysis (ICP-AES) was evaluated using the relative SD (RSD) of repeated determinations of the analytes. For all elements it ranged from 0.4 to 6%. The accuracy was evaluated on the basis of the analyte recoveries by spiking experiments. The recoveries and limits of detection values are listed in Table 3.

Table 3*. Limits of detection (LOD), line selection and recovery for the elements measured in the extract solution*

	Wavelength (nm)	Recovery (%)	LOD (µg/g)
Ag	328.068	99.6	0.0746
Al	308.215	91.2	0.0257
Ba	455.403	80.5	0.0405
Cd	214.441	95.4	0.0104
Co	228.615	98.9	0.0311
Cr	206.149	96.7	0.0680
Cu	224.700	98.4	0.1160
Fe	238.204	77.4	0.1170
Mg	285.213	81.9	0.1490
Mn	257.610	97.5	0.0064
Ni	231.604	90.0	0.0782
Pb	220.353	98.0	0.6750
Sr	407.771	83.2	0.0116
Zn	213.856	103.6	0.0983

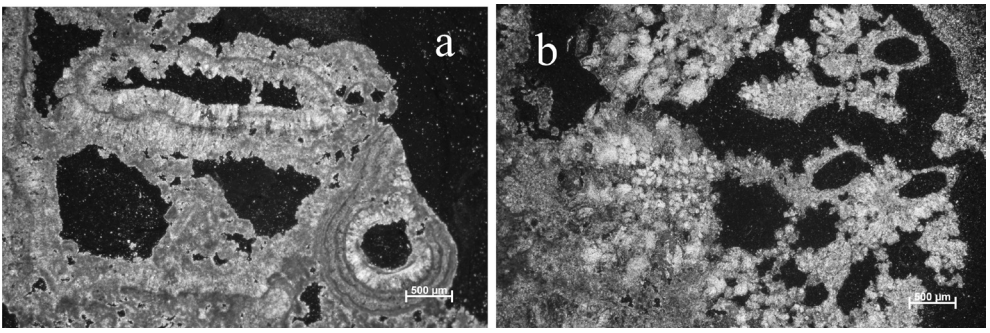

Fig. 2. *Thin-section photomicrographs (crossed nicols) of a mossy tufa showing micritic and microspar encrustations of micro- and macrophytes. Skradinski Buk waterfall. Sample K1*

The lowest recoveries were found for Fe, Mg, and Sr (77.4%, 81.9%, and 83.2%, respectively). In all extract solutions the concentrations of Ag, Al, Ba, Co, Cu, and Ni were below their limits of detection (0.0746, 0.0257, 0.0405, 0.0311, 0.116, and 0.0782 µg/g, respectively).
As regards the petrographic analysis, it was found on the basis of a framework of encrusted plant remains and porosity type that the studied tufas Tab.1 are similar in texture and composition to the deposits reported by Love & Chafetz (1988). Four specimens of brown to light brown colours were more or less friable, except the two shown on Fig.1 (a, b). Broadly, two major morphologies of sampled tufas have been distinguished in this active system, namely: a/ encrusted mossy deposits (Fig.1 a), and b/ algally laminated crusts (Fig.1 b). Aquatic mosses abound at the Skradinski Buk waterfalls, constructing the bulk of highly porous deposits. Hereby, moulds (Fig.1 a, c and d) readily visible in the form of numerous either regular or irregular cavities present in the rock testify to their former existence. In thin-section, mossy-type encrustations consist of microcrystalline aggregates composed of peloidal, clotted or structureless micrite, contributing to fragile structure (Fig.2 a, b). Additionally, partial occurrences of recrystallization (Fig.2 b) and pore-filling cements (Fig.1 e, f) are also present.

Fig. 1 b shows an in hand specimen of algally laminated crust. Is a hard and compact stratified rock composed of alternating dark and light laminations up to 2 and 4 mm thick, respectively. On a microscopic scale, these laminae are micritic and sparitic as a result of seasonal encrustation by different algal filaments (Fig.3) as well as diagenetic processes.

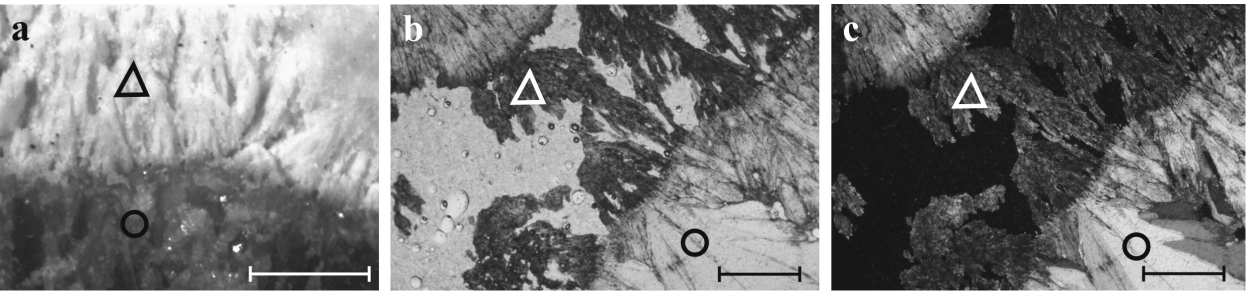

Fig. 3. *Algally laminated crust (specimen K3). (a) Stereo microscopic view of the contact between the light (triangle mark) and the dark (circle mark) laminae. Thin-section photomicrographs (b – plane light, c – crossed nicols) of laminae shown on (a). (c) Sparite fans (circle mark) corresponding to the dark lamina (shown on a) exhibit sweeping extinction, whereas the bushy-like light lamina (shown on a, triangle mark) is composed of micrite and appears dark when turning the table. Scale on all three figures is 1 mm long.*

Despite the difficulties in preparing a thin-section of specimen K4, it was possible to discern micritic and microspar layers, possibly formed by both inorganic and organic processes within mucilage sheath (Love, 1985). Some signs of re-crystallization and cementation were also observed.

Discussion

Relatively little research had been conducted on tufa deposits some 30-40 years ago, mainly due to their transient and localized nature (Love, 1985). However, recent ever growing investigations exploit freshwater tufa carbonates as geochemical archives of palaeoenvironmental change (Andrews, 2006; Ortiz et al., 2009; Brasier et al., 2010). The corresponding studies have been carried out for more than a decade in the Krka National Park (Horvatinčić et al., 2000; Lojen et al., 2004, 2009). Conventional ^{14}C ages of tufa samples from the Krka River with detailed description of the sampling sites were published in the Radiocarbon Data Lists (Srdoč et al., 1987, 1992; Horvatinčić et al., 1999). According to Horvatinčić et al. (2000) the large number of tufa samples dated by ^{14}C belongs to the time period from 6000 to 8000 yr B.P.

Accumulations of waterfall or cascade tufa deposits from the Krka River have been studied by this research? in order to provide the first petrographic report on their morphology, diagenesis and chemical composition of the carbonate phase. Field work was conducted exclusively on the Skradinski Buk waterfall which is the largest tufa barrier in Europe.

Commonly, freshwater carbonates exhibit a great variety of structures, textures, and morphologies, containing a wide diversity of constituents. This is evidenced by a heterogenous macroscopic description of the tufa samples listed in Table 1. These pecimens exhibit a wide range of textures, ranging from soil-like crumbly mass through the cake-like soft or hard crust to a lace-like hard and very porous rock (Fig.1). In spite of the small number of specimens, it can be said that there is an overall similarity between them and an adjacent Holocene tufa from the Zrmanja River studied by Pavlović et al. (2002 a, b). The mossy textural type (shown in Fig.1 a) is hard and porous, exhibiting wide range of fascinating constituents, either organic (Fig.1 c, d) or inorganic (Fig.1 e, f). A detail presented in Fig.1 a, (in frame) represents clear, rhombohedral crystals composing possibly meniscus cement (Fig.4).

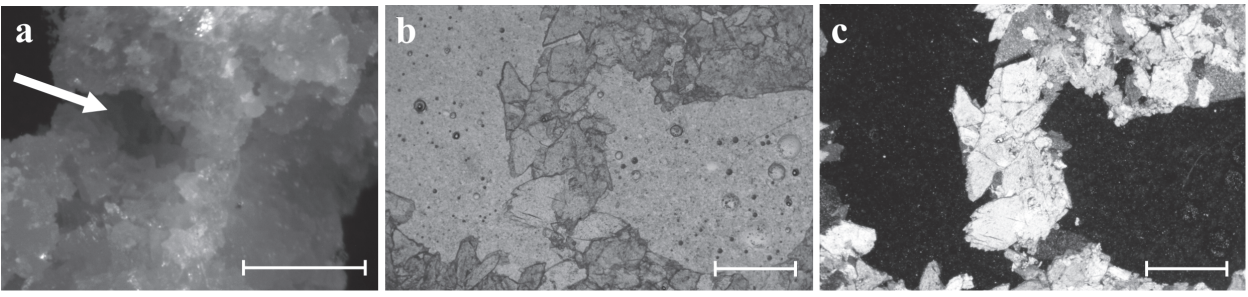

Fig. 4. *Encrusted mossy deposit (specimen K2). (a). Stereo microscopic view of the calcite crystals (arrow) as a part of the cementation process (in frame within the insert in Fig.1a). Thin-section photomicrographs (b – plane light, c – crossed nicols) of calcite crystals shown on (a). Scale on all three figures is 1 mm long*

Fig.1 b shows a sample of algally laminated crust. Is the hardest and densest sample in a whole series, composed of nearly parallel laminae. Those dark in hand specimens appear fine-grained, but in thin sections they are composed of bladed monocrystals, possibly calcifying microphytes' filaments (Fig.3 b, c). This can be interpreted as a result of aggradational neomorphism, forming coarse, columnar crystals enclosing cyanophyte filaments (Love & Chafetz, 1988). The authors attributed this sort of recrystallization to ammonia from decomposing algae.

A rough inspection of the measured variables values (Tab.2) demonstrates the generally low insoluble residue content and low metal concentrations characteristic for the precipitation in a freshwater environment. Due to the specific chemical method (Tessier et al., 1979; Cook, 1992) applied in this study it is somewhat difficult to compare the chemical data with previous investigations on the Krka River tufa deposits carried out on the whole rocks. However, it can be said that the data from this study are more or less similar to the data of the two studies (Frančišković-Bilinski et al., 2004; Cukrov & Lojen, 2010) for the majority of metals, except for Fe and Mn; hereby, previously obtained Fe and Mn values are substantially higher than the respective values in this study (Tab.2). This could be partially explained by somewhat lower recovery of Fe (Tab.3), but at the same time not for Mn; moreover, strong variabilities in acid soluble Fe- and Mn-contents of tufa deposits were found in some other studies (e.g. Irion & Müller, 1968; Pentecost, 1993). Thereby, Irion & Müller (1968) reported ranges (minimum-maximum) for Fe and Mn to be (in ppm) 46-3900, and 6-1600, respectively. Pavlović et al. (2002a) used the same chemical method as in this study, and reported the following ranges (minimum-maximum) for Fe and Mn (in ppm): 112-164, and 65-163, respectively. Nevertheless, Fe and Mn values (Tab.2) are certainly consistent with respect to the petrographic features of the precipitates. A textural departure of specimen K6 (Tab.1) from the others is reflected in its anomalously high values of Zn, Cr, and I.R., slightly increased levels of Fe, Mn, and O.M., and the second lowest values of Sr, Mg, and Pb. On the contrary, specimens K3 and K2 were the first and second with regard to hardness (Tab.1), having the lowest levels of Fe, Mn, and O.M., but the highest values of Sr and Mg (Tab.2). Cipriani et al. (1972) proposed that the insoluble residue in tufas could be either a syngenetic or a postgenetic feature based on its correlation with Sr. In the latter case, calcite should be devoid of its original Sr-content, so that the correlation Sr-I.R. would be negative; also, correlations among Fe (Mn) and Sr (Mg) would be negative. In fact, Sr and Mg coprecipitate with Ca in calcite (Veizer, 1983), whereas their decreased values are indicative of later diagenetic processes operating in karstic environment, generally contributing to the increased I.R. content. Fe^{2+} and Mn^{2+}, resulting from the microbial oxidation of O.M., possibly migrate from the I.R. particles into a diagenetic carbonate phase. Such statements, regarding relations among metals (Fe, Mn, Sr, and Mg) and I.R. and O.M., are in agreement with the results listed in Table 4. It must be noted that coherent relations were found for the majority of tested pairs in both groups (i.e. n = 6, and 4), except for Pb and Cr (underlined in Tab.4), thus suggesting that there is an overall chemical trend in analysed tufa samples, regardless of their petrographic features.

Nevertheless, the well-known diversity of environments and microenvironments existing within the overall tufa-depositing environment certainly warrants more samples covering all present morphologies, as well as the coordination with biologists.

Conclusions

Tufa deposits from the Krka River were studied in order to present the petrographic description of their morphology and texture, together with the chemical composition of their carbonate phase. Generally, tufa samples have been classified into two types: 1/ mossy deposits and 2/ algally laminated crusts. Carbonate phase is composed of calcite, whereas the insoluble resi-

Table 4. *Kendall's Tau correlation matrix for all six samples, and after the exclusion of the samples K3 and K6 (in italics); numbers in bold are significant at p < 0.05 (n = 6 and 4, respectively)*

	Fe		Mn		Sr		Mg		Zn		Pb		Cd		Cr		O.M.		I.R.	
Fe	1,00	*1,00*																		
Mn	**0,87**	*0,67*	1,00	*1,00*																
Sr	**-0,73**	***-1,00***	-0,60	*-0,67*	1,00	*1,00*														
Mg	-0,60	***-1,00***	-0,47	*-0,67*	0,60	***1,00***	1,00	*1,00*												
Zn	0,20	*0,00*	0,33	*0,33*	0,07	*0,00*	-0,33	*0,00*	1,00	*1,00*										
Pb	0,07	***1,00***	-0,07	*0,67*	-0,07	***-1,00***	-0,47	***-1,00***	0,07	*0,00*	1,00	*1,00*								
Cd	-0,28	*-0,33*	-0,41	*-0,67*	0,28	*0,33*	0,41	*0,33*	-0,28	*-0,67*	-0,28	*-0,33*	1,00	*1,00*						
Cr	0,20	*0,00*	0,33	*0,33*	0,07	*0,00*	-0,33	*0,00*	**1,00**	***1,00***	0,07	*0,00*	-0,28	*-0,67*	1,00	*1,00*				
O.M.	**0,87**	*0,67*	**0,73**	*0,33*	-0,60	*-0,67*	-0,47	*-0,67*	0,07	*-0,33*	-0,07	*0,67*	-0,14	*0,00*	0,07	*-0,33*	1,00	*1,00*		
I.R.	0,55	*0,33*	0,69	*0,67*	-0,28	*-0,33*	-0,41	*-0,33*	0,69	*0,67*	0,00	*0,33*	-0,64	***-1,00***	0,69	*0,67*	0,41	*0,00*	1,00	*1,00*

due averaging 3.70% contains quartz, 10 Å phyllosilicate (illite and/or mica), chlorite, K-feldspar, amphibole and smectite. Statistically significant Kendall's Tau correlations (at $p < 0.05$) were found for the following pairs of variables: Fe-Mn (0,87), Fe-Sr (-0.73, or <-0.99), Fe-Mg (<-0.99), Fe-O.M. (0.87), Mn-O.M. (0.73), Sr-Mg (>0.99), Zn-Cr (>0.99), and Cd-I.R. (<-0.99). Negative correlation between Sr and I.R. could indicate that it resulted from the karstic weathering processes. Trace metal concentrations in the carbonate phase were low according to a freshwater environment of precipitation, with median values as follows: (in µg/g): 5.98 (Fe), 18.75 (Mn), 95.10 (Sr), 582.50 (Mg), 3.52 (Zn), 2.42 (Pb), 1.05 (Cd), and 3.35 (Cr). Textural features like recrystallization and cementation were accompanied by increased Sr and Mg, and decreased Fe, Mn and I.R. values; on the contrary, possible karstic weathering processes are evidenced by decreased Sr and Mg, and increased Fe, Mn, and I.R. levels.

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ХИМИЧЕСКИ СЪСТАВ И ТЕКСТУРА НА БИГОРА В ДОЛИНАТА НА РЕКА КРКА В ДИНАРСКИЯ КАРСТ, ХЪРВАТИЯ

Medunić G.[1], Juranović Cindrić I.[2], Pivčević N.[1], Kampić Š.[1], Prohić E.[1], Goreta G.[3], Čobić A.[1]

[1] Институт по минералогия и петрология, Факултет по науки, Загребски университет, Хърватия

[2] Лаборатория по аналитична химия, Факултет по науки, Загребски университет, Хърватия

[3] Национален парк Крка, Национален институт, Шибеник, Хърватия

Резюме. Бигорът – скала от карбонати седименти от сладководни органични и неорганични процеси – е широко разпространен в Националния парк Крка (Кърка) в Динарския карст, Хърватия, където формира стари и съвременни водопади. Проведени са химически, петрографски и статистически анализи на бигорни образци от шест представителни места с цел текстурата и микроелементният състав на бигора да се свържат с геохимичните процеси, които протичат в тази разнообразна среда. Металните микроконцентрации в карбонатната фаза са анализирани по метода ICP-AES след еднократно извличане с 1M Na-ацетат. Неразтворимият остатък (I.R.), който варира от 2.20 до 21.10 % (средно 3.70 %), би могъл да бъде резултат от карстовите денудационни процеси, влияещи на химическия състав на бигорните образци. Като цяло, увеличеното съдържание на Fe, Mn и I.R. е свързано с намалено съдържание на Sr и Mg, и обратно.

Ключови думи: *бигор, последователно извличане (екстракция), мъхова инкрустация, корелация на метални микроконцентрации, ре-кристализация, река Крка*

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