Journal of Geochemical Exploration 167 (2016) 20–37

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/gexplo

Geochemical and mineralogical characterization of speleothems from the karst of Croatia as potential sources of data for environmental researches

Dalibor Paar [a,*], Stanislav Frančišković-Bilinski [b], Nenad Buzjak [c], Krešimir Maldini [d], Simana Milović [d], Srđan Pichler [e]

[a] University of Zagreb, Faculty of Science, Department of Physics, Bijenička c. 32, HR 10000, Zagreb, Croatia
[b] Ruđer Bošković Institute, Bijenička c. 54, HR 10002, Zagreb, Croatia
[c] University of Zagreb, Faculty of Science, Department of Geography, Marulićev trg 19/II, HR 10000, Zagreb, Croatia
[d] Croatian Waters, Central Water Management Laboratory, Vukovarska 220, HR 10000, Zagreb, Croatia
[e] Fund for Financing the Decommissioning of NEK, Radnička c. 47, HR 10000, Zagreb, Croatia

ARTICLE INFO

Article history:
Received 14 November 2015
Revised 3 May 2016
Accepted 8 May 2016
Available online 16 May 2016

Keywords:
Speleothems
Geochemistry
Mineralogy
Trace elements
Paleoenvironment
Karst
Croatia

ABSTRACT

The aim of this study is to detect proxies from speleothems that are suitable for geochemical and paleoenvironmental research in Croatian karst (Dinaric karst and isolated karst of the Pannonian basin). The main subject is elemental composition and mineralogy of speleothems from various sites in Croatian karst and whether the different climatic, geological and hydrological characteristics of those karst regions affect elemental and mineralogical characteristics of speleothems in order to design and plan future research. Total of 37 speleothem samples from 32 caves in different geological, geomorphological and climatic zones of Croatian karst were collected. In all samples concentration of 30 elements was determined by ICP-MS and mineral composition was analyzed by XRD. In 82% of studied samples calcite is the only mineral identified. Minor minerals detected are: quartz, dolomite, muscovite/illite, chlorite and plagioclase. Besides the most abundant calcium, the elements with the highest concentrations (>500 mg/kg) are: Al, Fe, Si and Mg. Elements with the lowest concentrations recorded (<1 mg/kg) are: Be, Cd, Tl, W, Bi, U, As and Co. Besides Cd, other heavy metals used as anthropogenic contamination indicators have very low concentrations (<10 mg/kg). Statistical relationships between elements were established. A boxplot statistical method showed that largest numbers of anomalies are present in all three samples from Lukina jama located on Northern Velebit Mountain, where a whole series of elements, including many heavy metals, show extreme values (Pb, Cu, Zn, Mn, Ni, Cr, Co, Ba, K, Mg, Li, Be, Al, U, Si, Ti, W, Fe, As). Factor analysis showed that anomalies of element concentrations in most cases can be explained by local mineralogical conditions. This study will significantly contribute the knowledge about elemental and mineralogical composition of speleothems in Croatia, which are mostly determined by geogene influence.

1. Introduction

The speleothems (from Greek *spelaion* = cave and *thema* = deposit) are secondary mineral deposits (mostly calcite and aragonite) found in caves and artificial cavities in karst areas. The minerals that form speleothems deposit from dripping water, from thin sheets of water, at cave lakes and pools rims and even under fresh water. They occur in a variety of different forms, structures and mineralogy (Hill and Forti, 1997; Fairchild and Baker, 2012). Speleothems are valuable archives of past environmental conditions characterized by their large geographic extent and extensive growth intervals. They contain geochemical and paleoenvironmental data and therefore represent one of the front lines in research of paleoprocesses and paleoenvironments. Their advantage compared to other sources is a multitude of "proxy" records both directly and indirectly linked to climatic fluctuations, they are typically robust, and display a high preservation potential with no post-depositional alteration because they preserve fluctuations in trace element chemistries of their formation waters, host rock and even surface systems (soils, aerosols in atmosphere). These geological materials are characterized by a relatively simple internal stratigraphy that reflects their growth history and geochemical changes through that history influenced by various environmental factors like geological composition, geomorphological processes, hydro(geo)logical conditions, pedological composition, climate, vegetation and anthropogenic impact (Fairchild and Treble, 2009; Fairchild and Baker, 2012; Oster et al., 2012). The lithology, geological relationships determined by tectonic movements and hydrological conditions of the rock layers overlying the cave, geomorphological properties of the cave and cave hydrology, ecosystem(s), climate and soil zone of the surface and near the surface have

* Corresponding author.
E-mail address: dpaar@phy.hr (D. Paar).

http://dx.doi.org/10.1016/j.gexplo.2016.05.004
0375-6742/

important influence on speleothem accumulation, composition and, in some cases, destruction too. Their characteristics can show characteristic variations with time and imprint of these changes can be read from speleothem stable isotope and trace elements composition (Fairchild et al., 2006; Wu et al., 2015). Speleothems can also be used as geochemical tracers of water-rock interactions (Verheyden, 2004). Trace element variations in speleothems can also be interpreted as indicators of changes in paleo-rainfall and hydrologic conditions (Tremaine and Froelich, 2013). The ecosystem and soil zone overlying the cave fundamentally imprint the carbon and trace element signals and can show characteristic variations with time (Fairchild et al., 2006). It is also known that speleothems could be used as archives of anthropogenic influence, e.g. pollution after increase of trace elements (Dandurand et al., 2011; Allan et al., 2015). The aim of in situ studies is to differentiate influences, such as climate, soil/weathering and local hydrology in order to better constrain possible transfer functions between the surface and a speleothem (Verheyden, 2004; Borsato et al., 2007; Fairchild and Treble, 2009; Fairchild and Baker, 2012). For this kind of research, the most interesting is the vadose (unsaturated) zone, where speleothems in karst are deposited. It extends from the top of the ground surface to the water table in phreatic (saturated) zone (Ford and Williams, 2007). Its evolution and conditions important for speleothem depositions are controlled by geological composition and structures, geomorphological processes, soils and residual deposits from the surface and host rocks.

Before a demanding analysis of individual speleothem and chronological analysis of paleoclimatic and paleoenvironmental data, it is necessary to have an overview of the general geochemical and mineralogical properties of speleothems that are available, whether they contain adequate proxies and whether the average concentration of proxies changes if we change the location, not only in respect of climatic and geological characteristics of the area where the cave is located, but also within the cave. This paper aims to obtain first such data in Croatian karst as such investigations have not been performed in Croatia before. Croatian karst is specific in a way that at a relatively small area there are different climatic, geological, geomorphological and pedological zones and processes influencing speleogenesis, speleothem growth and composition. The differences analysis in the properties of speleothems between the sites therefore may be methods that detect proxy suitable for studying paleoclimatic and other environmental processes. In addition, a lot of speleothems are not suitable for paleoenvironmental studies due to non-equilibrium conditions during deposition or their structure. The analyses of 30 elements and mineralogical composition carried out show specificity in their elemental composition which allows further analysis and integration into the wider picture of the impact of geological and climatic conditions in the past.

Up to now speleothem research in Croatia has been related to the study of environmental changes and speleogenesis (Babić et al., 1996; Lacković et al., 2011), coastal karst evolution, changes in sea level, and climate change (Surić et al., 2005a, 2005b, 2009, 2010; Rudzka et al., 2012), but elemental and mineralogical analyses have not been performed yet.

The karst occupies almost 44% of the Croatian mainland and islands (submerged karst of the Adriatic Sea not included; Bognar et al., 2012). According to morphogenetic characteristics it is divided into three morphogenetic types: karst (39%), fluviokarst (3%), and glacial and periglacial relief developed on karst terrains of Dinaric mountains (2%). According to the differences in geological composition and geomorphological processes it includes two karst geospatial units. The larger and dominant unit of *Dinaric karst belt* is formed in >8 km thick carbonate rocks deposited in several episodes beginning with the Upper Paleozoic and continuing through the Mesozoic and Tertiary and deformed by intense geodynamics (Vlahović et al., 2005; Korbar, 2009). According to their characteristics it can be divided to three subunits. *Dinaric Mountains subunit* is of the highest elevations (range 1500–1831 m a. s. l.), characterized by the intense and deep karstification, deep vadose zone (a depth of about 1500 m below surface) with steep conduits towards deep karst aquifers (Kuhta and Bakšić, 2001; Bočić, 2006). It is the transitional area of temperate (*Cfb*) and moist continental climate with cold winters (*Df*), characterized by precipitation range 1100–3500 mm/y (Fig. 1). The vadose zone in the areas of *karst plains and karst poljes subunit* has mostly shallower vadose zone (mostly up to 100 m below surface) but also generally characterized by typical karst conduit porosity, with often spatial exchange between bare and covered karst influenced by climate, vegetation and anthropogenic impact. *The coastal karst subunit* is characterized by intensive water interactions between the sea and the coast through submarine groundwater discharge (SGD) into the sea and seawater intrusion into the coastal aquifers (Surić et al., 2015). It is the area of transition from Mediterranean (*Cs*) to temperate climate (*Cfa*) towards NW and inlands. The precipitation range is the lowest on the southern islands (300–800 mm/y) and increases towards NW, inland and with elevation rise (700–1200 mm/y). The second geospatial unit is *isolated karst of Pannonian basin and border zone towards Dinarides*. It is characterized by a shallow vadose zone, less abundant karst phenomena, larger areas of fluviokarst and more intensive anthropogenic impacts resulting in generally compromised environmental issues. It is the area of covered karst with thicker soil cover, abundant vegetation typical for temperate climate (*Cfb*) with precipitation range 800–1100 mm/y (Filipčić, 1998; Zaninović et al., 2008).

Most of speleothem studies are concentrated on the research of specific sample with a limited number of proxies. The aim of this paper is to provide a broad overview of potential proxies based on trace elements and mineralogical analysis that could be used in further research and may indicate the proxies that were not considered in previous studies and can provide new information on paleoenvironmental conditions. The aim of research was to determine geochemical composition (elements and minerals) of speleothems from various sites in Croatian karst (Dinaric karst and isolated karst of the Pannonian basin), as well as possible relationships between them and environmental conditions (geological, geomorphological, pedological, hydrogeological, climate and possible anthropogenic influence). So, there is a question whether the different climatic and geological characteristics of karst regions affect geochemical and structural characteristics of speleothems. In this discussion we should take into account parameters such as location of speleothem inside the cave, specific hydrological, local geological conditions and geochemistry of parent rocks where the selected caves developed. But, unfortunately, such data are almost inexistent for the investigated locations. It is also important to stress that the amounts of minor and trace metals coprecipitated into calcite and aragonite are a record of the (paleo)environment during crystallization. We analyzed differences between the sites in order to indicate links between the specifics of individual locations (Fig. 1; Table 1).

All samples were subjected to the ICP-MS and X-ray diffraction analysis, and the results were statistically analyzed. This study will later enable the assessment of the influence of the above listed environmental conditions on the speleothem growth and composition, and their use in interpretation of paleoenvironmental conditions.

2. Materials and methods

2.1. Sampling of speleothems

Because of ethical and nature protection reasons we collected samples in a way that does not alter the appearance of the cave or already broken speleothems. In our study we primarily used calcite speleothems: stalactites (depositing down from the cave ceiling), one stalagmite (deposited up from the cave floor) and one phreatic speleothem (deposited in a phreatic environment). We chose caves that are typical of certain areas that have differences in some geological or climate properties. Most of the caves (91%) are located in the Dinaric

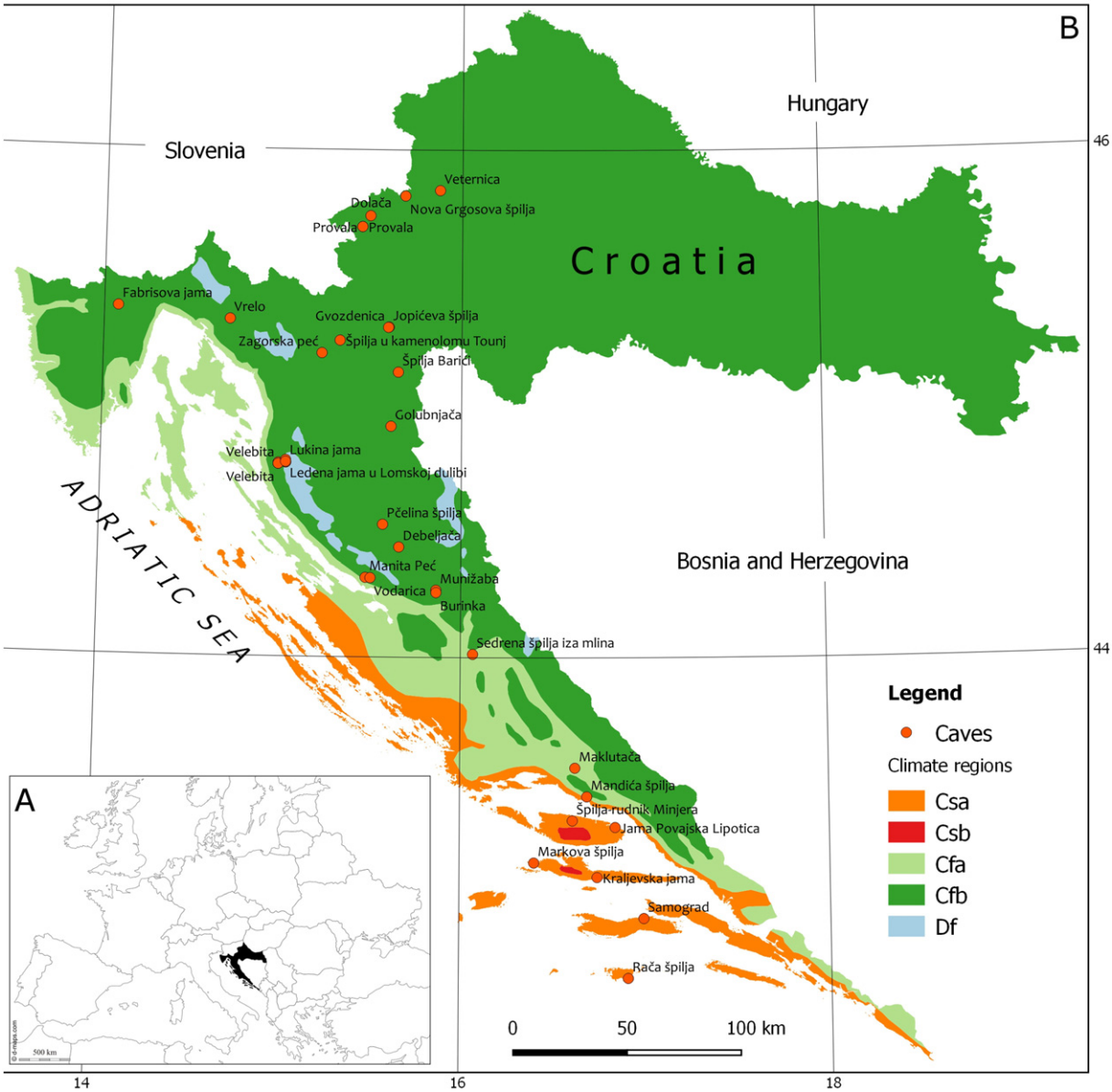

Fig. 1. A – Geographical position of Croatia in Europe. B - Locations of caves where speleothems were sampled on a climate map of Croatia after Köppen-Geiger climate classification. Legend: Csa - Mediterranean (temperate) climate with dry and hot summer, Csb - Mediterranean (temperate) climate with dry and warm summer, Cfa - temperate humid climate with hot summer, Cfb - temperate humid climate with warm summer, Df – cold humid boreal climate (Filipčić, 1998; Peel et al., 2007).

karst belt. Such spatial distribution is relevant since most of the up to now known caves in Croatia are located in this karst geospatial unit. Most of them are located in areas of complex geological composition mainly of carbonate beds (Zupan Hajna, 2011), with large amount of paleo- and recent carbonate precipitation (Surić et al., 2005a, 2005b, 2009, 2010), and characterized by a typical karst drainage network (Bonacci, 1987), so all basic conditions for speleothem growth are met. Elevation range of the researched caves is 63–1595 m a.s.l. According to hypsometric classes there are 6 caves in the class <200 m a.s.l., 14 caves 200–500 m, 7 caves 500–1000 m and 5 caves in the class of >1000 m. Samples were collected at location in different positions inside the caves with respect to the distance from the entrance and depth below the surface. The deepest sampling points were in Lukina jama-Trojama vertical cave system (shorter: Lukina jama), at 940 m and 1300 m below the surface (Fig. 2). Speleothems were sawn or broken off the rock.

2.2. Sample preparation and analysis

Speleothems were carefully handled and kept in separate plastic bags, to avoid possible cross-contamination. Before further sample preparation, speleothems were washed three times in distilled water and then dried at the room temperature. After that they were crushed and homogenized in a Retsch RM 200 mortar grinder and hand mortar. Whole speleothems specimens collected for analysis were crushed, to get an average sample containing all layers of speleothem, as each speleothem can encompass up to tens of thousands of years of precipitation, with several climate and environmental settings. Each speleothem sample was of another weight, some of them over 1 kg. From obtained powder, a representative sample of about 1 g was taken, which was sufficient to perform ICP-MS and XRD analysis. Approximately 0.1 g of powdered speleothem samples was dissolved with 2.5 ml of suprapur nitric acid and 7.5 ml of puriss hydrochloric

Table 1
Location of the caves – sampling locations.

Sample	Cave name	Location	HTRS96/TM E	HTRS96/TM N	Elevation (m)	Karst unit[a]	Climate type	Annual precipitation (mm/m^2)	Type[b]	Depth (m)
ZSDV-0001	Jopićeva špilja	Kordun region	428859	5018301	202	Dkb	Cfsbx”	1100–1200	A	<100
ZSDV-0003	Lubuška jama	Velebit Mt.	383499	4959167	1495	Dkb	Dfsbx”	1750–2000	A	250
ZSDV-0005	Špilja-rudnik Minjera	Brač Island	509033	4801898	246	Dkb	Csa	1000–1100	A	<100
ZSDV-0006	Dolača	Žumberak Mt.	420854	5067156	405	ikPb	Cfwbx”	1100–1200	A	<100
ZSDV-0007	Golubnjača	Lika region	429620	4974809	460	Dkb	Cfsbx”	1300–1400	B	<100
ZSDV-0009	Maklutača	Middle Dalmatia	510149	4824998	430	Dkb	Csbx”	1300–1400	A	<100
ZSDV-0010	Provala	Žumberak Mt.	417314	5062384	274	Dkb	Cfwbx”	1000–1100	A	<100
ZSDV-0011	Lukina jama	Velebit Mt.	383409	4959481	1475	Dkb	Dfsbx”	1750–2000	A	940
ZSDV-0018	Markova špilja	Hvar Island	492111	4783420	63	Dkb	Csa	700–800	A	<100
ZSDV-0039	Mandića špilja	Middle Dalmatia	515368	4812429	170	Dkb	Cfsax”	1000–1100	A	<100
ZSDV-0040	Manita Peć	Velebit Mt.	418249	4908756	575	Dkb	Cfsbx”	1750–2000	A	<100
ZSDV-0044	Munižaba	Velebit Mt.	449257	4903062	905	Dkb	Cfsbx”	2000–2500	A	350
ZSDV-0045	Rača špilja	Lastovo Island	533623	4732836	132	Dkb	Csa	600–700	A	<100
ZSDV-0046	Vodarica	Velebit Mt.	420417	4908602	695	Dkb	Cfsbx”	1750–2000	A	<100
ZSDV-0048	Jama Povajska Lipotica	Brač Island	527818	4799029	69	Dkb	Csa	1000–1100	A	<100
ZSDV-0053	Lukina jama	Velebit Mt.	383409	4959481	1475	Dkb	Dfsbx”	1750–2000	A	1300
ZSDV-0054	Zagorska peć	Kapela Mt.	399417	5007110	325	Dkb	Cfsbx”	1500–1750	A	<100
ZSDV-0055	Provala	Žumberak Mt.	417314	5062384	280	Dkb	Cfwbx”	1000–1100	A	<100
ZSDV-0056	Gvozdenica	Kordun region	428593	5018181	218	Dkb	Cfsbx”	1100–1200	A	<100
ZSDV-0058	Sedrena špilja iza mlina	Krka river	465347	4874918	201	Dkb	Cfsax”	1100–1200	A	<100
ZSDV-0059	Debeljača	Lika region	433002	4921849	747	Dkb	Cfsbx”	1500–1750	A	<100
ZSDV-0060	Nova Grgosova špilja	Samoborsko gorje Mt.	436151	5075761	242	ikPb	Cfwbx”	1100–1200	A	<100
ZSDV-0064	Samograd	Korčula Island	540460	4759098	75	Dkb	Csa	900–1000	A	<100
ZSDV-0065	Špilja Barići	Kordun region	432870	4998522	265	Dkb	Cfwbx”	1200–1300	A	<100
ZSDV-0066	Burinka	Velebit Mt.	449295	4902027	815	Dkb	Cfsbx”	2000–2500	A	250
ZSDV-0070	Fabrisova jama	Istra peninsula	310254	5028447	384	Dkb	Cfsbx”	1400–1500	A	<100
ZSDV-0072	Pčelina špilja	Lika region	425908	4931829	780	Dkb	Cfsbx”	1500–1750	A	<100
ZSDV-0074	Kraljevska jama	Hvar Island	519898	4777058	144	Dkb	Csa	900–1000	A	140
ZSDV-0075	Vrelo	Gorski kotar region	359225	5022306	722	Dkb	Cfsbx”	2500–3000	A	<100
ZSDV-0076	Meduza	Velebit Mt.	380206	4959143	1595	Dkb	Dfsbx”	1750–2000	A	250
ZSDV-0077	Jamski sustav Velebita	Velebit Mt.	380160	4958622	1557	Dkb	Dfsbx”	1750–2000	A	860
ZSDV-0078	Jamski sustav Velebita	Velebit Mt.	380160	4958622	1557	Dkb	Dfsbx”	1750–2000	A	880
ZSDV-0081	Jamski sustav Velebita	Velebit Mt.	380160	4958622	1557	Dkb	Dfsbx”	1750–2000	A	860
ZSDV-0082	Ledena jama u Lomskoj dulibi	Velebit Mt.	383428	4960274	1235	Dkb	Dfsbx”	1750–2000	A	50
ZSDV-0083	Lukina jama	Velebit Mt.	383409	4959481	1475	Dkb	Dfsbx”	1750–2000	A	1300
ZSDV-0084	Špilja u kamenolomu Tounj	Tounj	407359	5012597	251	Dkb	Cfsbx”	1400–1500	C	<100
ZSDV-0085	Veternica	Medvednica Mt.	451345	5078104	317	ikPb	Cfwbx”	1000–1100	A	<100

[a] Dkb = Dinaric karst belt, ikPb = isolated karst of Panonnian basin.
[b] A - stalactite, B - stalagmite, C- phreatic speleothem.

acid for half an hour at 1000 W in Anton Paar Multiwave 3000 Oven according to ISO 11466 norm. Dissolved samples were quantitatively transferred to volumetric flasks and diluted to 50 ml with deionised water. All laboratory glassware were submerged for 24 h in 1% HNO_3 solution and rinsed three times with deionised water prior to use. Calibration lines for each element and internal standards were made using Perkin Elmer Multi-element calibration standard solution.

The elements contents were detected by inductively coupled plasma-mass spectrometry (ICP-MS, Elan 9000, Perkin Elmer, USA), with solution of 20 μg l^{-1} Ge, Rh, In and Re as internal standard according to HRN EN ISO 17294–1 and HRN EN ISO 17294–2 norms. All measurements were performed in triplicates. The precision, evaluated directly as the relative standard deviation (RSD), was better than 10% for all determined elements. The accuracy of the ICP-MS analytical procedure and method quality control was performed by the analysis of the elements of interest in standard reference material (RTC, Trace elements on fresh water sediment, catalog number: CNS392-050), which were analyzed at the beginning and after analyzing each series of samples. A generally good agreement within 15% was observed between our data and the certified values. Limit of quantification is the lowest quantity of analyte in a sample that can be quantified with an acceptable level of accuracy and precision, calculated by multiplying the standard deviation of 10 measurements of a certain sample by 10, or by multiplying the value of the limit of detection by 3.3. The results of ICP-MS measurements show only two values below the limit of quantification – for the element Tl in two samples, ZSDV-64 and ZSDV-70, which is 5.4%.

Determination of mineralogical composition of speleothems was done using X-ray diffractometer Philips, X-Pert MPD (start position: 82Q: 4.01; end position: 82Q: 62.99; generator settings: 40 kV, 40 mA). Crystalline phases were identified using a Powder Diffraction File (1997) and computer program X'Pert High score 2002, Philips. Semi quantitative mineralogical composition was determined as described in Boldrin et al. (1992).

2.3. Statistical analysis

All statistical analyses were obtained using program Statistica 6.0 (StatSoft, 2001). The following statistical analyses were performed:

a) Determination of basic statistical parameters: N (number of cases), mean, geometric mean, median, mode, frequency, minimum, maximum, standard deviation, skewness, and kurtosis. These parameters were determined to present a closer view to the experimentally determined values, without presenting the whole dataset. Correlation analysis was performed by calculating Pearson's correlation coefficient and presented in the form of correlation matrix to determine the strength of linear correlation of mass fractions between

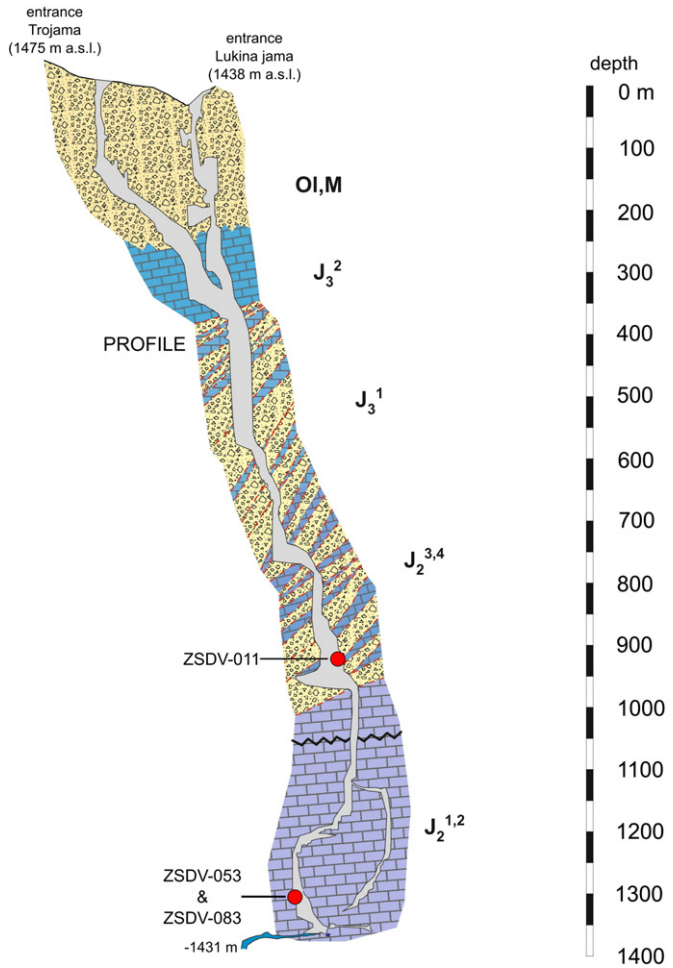

Fig. 2. Sampling locations in Lukina jama-Trojama system, North Velebit NP (Stroj and Velić, 2015). Legend: $J_2^{1,2}$ – limestones (Middle Jurassic); $J_2^{3,4}$ - Velebit limestone breccia & limestone (Middle Jurassic); J_3^1 – Velebit limestone breccia & limestone (Upper Jurassic); J_3^2 – dolomitic limestones (Upper Jurassic); Ol, M - Velebit limestone breccia; red line – fault, approximate position.

researched elements. Obtained values were statistically significant at $p < 0.05$.

b) Boxplot method was used to determine anomalies in sediment samples. Normal or lognormal box-plots are constructed on the basis of the empirical cumulative distribution plots. The box length was of interquartile range, where outlier values were defined between 1.5 and 3 box lengths from the upper or lower edge of the box. Extremes are values >3 box lengths from the edge of the box (Tukey, 1977; Reimann et al., 2005).

c) Cluster analysis of Q-mode was performed to find groups which contain similar samples. Cluster analysis belongs to multivariate statistics and represents a hierarchical method. There are two modes of cluster analysis: Q-mode, in which clusters of samples are sought, while in the R-mode clusters of variables (in our case, elements) are desired (Kaufman and Rousseeuw, 1990).

d) Factor analysis was also performed in order to reduce the number of variables and to set up a model of several factors, each of them describing one anthropogenic or natural influence. In factor analysis, the relation between a set of m variables is assumed to reflect correlations of every one of the variables with p mutually non-correlated main factors. The general assumption is that $p < m$. Variance of m variables is derived from the variance of the p factor (Halamić et al., 2001; Davis, 2002).

3. Results

3.1. Semiquantitative mineralogical analysis

Results of semiquantitative mineralogical analysis are presented in Table 2. In 31 of total 37 studied samples (83.8%) calcite is the only mineral identified by XRD method. This does not necessarily mean that traces of other minerals do not exist, as detection limit of this method is ~2%, and traces of other minerals could be present. In only 6 samples (16.2%) some other minerals besides calcite have been detected. Also, in those samples calcite abundance is over 90%, while other minerals are accessory minerals, which are present in small amounts around value of detection limit. Among them, three samples are from Lukina jama, taken at different positions (with respect to depth). In those three samples, besides calcite, the following minerals have been detected: quartz, muscovite/illite, chlorite and plagioclase. Illite and chlorite indicate clays – the most common insoluble components in carbonate rocks. There are two main sources of clays in caves: allogenic and authigenic (Ford and Williams, 2007). Allogenic sources in this case could include flushing or infiltration from soils and reworked fluvial infillings. Authigenic source is rock weathering. In case of sample ZSDV-0011 and samples ZSDV-0053 and ZSDV-0083 the main source could be reworked fluvial deposit since samples ZSDV-0053 and ZSDV-0083 were taken from the epiphreatic zone where by logger recorded water level oscillations exceed 100 m (Paar et al., 2012). Sample ZSDV-0011 was taken from top of the chamber with water stream and where geomorphological traces of (paleo) floods were observed (accumulated fluvial sediments: silt, sand and gravel). During flood events fine-grained sediments including clay are deposited around the cave passage perimeter. Due to the bare karst surface with some limited soil pockets (up to

Table 2
Mineral (phase) composition of speleothem samples.

Sample	Mineral (phase) composition	Sample	Mineral (phase) composition	Sample	Mineral (phase) composition
ZSDV-0001	Calcite	ZSDV-0046	Calcite	ZSDV-0072	Calcite
ZSDV-0003	Calcite	ZSDV-0048	Calcite	ZSDV-0074	Calcite
ZSDV-0005	Calcite	ZSDV-0053	Calcite, quartz, muscovite/illite, chlorite	ZSDV-0075	Calcite, dolomite
ZSDV-0006	Calcite	ZSDV-0054	Calcite, dolomite	ZSDV-0076	Calcite
ZSDV-0007	Calcite	ZSDV-0055	Calcite	ZSDV-0077	Calcite
ZSDV-0009	Calcite	ZSDV-0056	Calcite	ZSDV-0078	Calcite
ZSDV-0010	Calcite	ZSDV-0058	Calcite	ZSDV-0081	Calcite
ZSDV-0011	Calcite, quartz, clorite, muscovite/illite	ZSDV-0059	Calcite	ZSDV-0082	Calcite
ZSDV-0018	Calcite	ZSDV-0060	Calcite	ZSDV-0083	Calcite, quartz, chlorite,
ZSDV-0039	Calcite, quartz	ZSDV-0064	Calcite		Muscovite/illite, plagioclase
ZSDV-0040	Calcite	ZSDV-0065	Calcite	ZSDV-0084	Calcite
ZSDV-0044	Calcite	ZSDV-0066	Calcite	ZSDV-0085	Calcite
ZSDV-0045	Calcite	ZSDV-0070	Calcite		

Table 3
Results of ICP-MS analysis of 30 chemical elements.

Sample	Cd mg/kg	Pb mg/kg	Cu mg/kg	Zn mg/kg	Mn mg/kg	Ni mg/kg	Cr mg/kg	Co mg/kg	Ba mg/kg
ZSDV-0001	0.018 ± 0.001	0.237 ± 0.003	0.487 ± 0.011	2.93 ± 0.026	1.30 ± 0.036	1.61 ± 0.045	0.509 ± 0.043	0.590 ± 0.024	3.82 ± 0.084
ZSDV-0003	0.063 ± 0.003	1.25 ± 0.038	0.756 ± 0.010	3.51 ± 0.046	2.85 ± 0.077	3.83 ± 0.088	2.59 ± 0.053	0.551 ± 0.009	12.8 ± 0.179
ZSDV-0005	0.371 ± 0.004	0.413 ± 0.005	0.875 ± 0.004	2.29 ± 0.015	2.82 ± 0.034	2.63 ± 0.068	0.780 ± 0.051	0.744 ± 0.015	1.80 ± 0.009
ZSDV-0006	0.029 ± 0.0006	0.367 ± 0.013	0.542 ± 0.011	1.88 ± 0.023	5.22 ± 0.026	1.71 ± 0.105	0.881 ± 0.019	0.980 ± 0.013	8.67 ± 0.078
ZSDV-0007	0.092 ± 0.003	1.16 ± 0.020	1.40 ± 0.020	5.25 ± 0.063	23.5 ± 0376	3.76 ± 0.086	1.70 ± 0.040	0.937 ± 0.030	4.08 ± 0.102
ZSDV-0009	0.078 ± 0.005	15.73 ± 0.267	1.55 ± 0.011	5.34 ± 0.053	13.0 ± 0.143	2.36 ± 0.066	1.23 ± 0.014	0.695 ± 0.017	2.89 ± 0.92
ZSDV-00010	0.019 ± 0.001	0.289 ± 0.004	0.537 ± 0.002	1.39 ± 0.024	1.86 ± 0.024	1.85 ± 0.085	1.0 ± 0.045	0.637 ± 0.010	3.91 ± 0.086
ZSDV-00011	0.545 ± 0.013	14.0 ± 0.084	9.97 ± 0.119	26.5 ± 0.291	255 ± 3.82	31.6 ± 2.96	18.8 ± 0.180	5.09 ± 0.025	80.9 ± 1.37
ZSDV-00018	0.121 ± 0.0009	2.18 ± 0.033	1.29 ± 0.019	5.96 ± 0.036	8.68 ± 0.061	1.74 ± 0.036	1.01 ± 0.106	0.619 ± 0.006	13.0 ± 0.208
ZSDV-00039	0.222 ± 0.003	0.954 ± 0.006	9.31 ± 0.074	26.9 ± 0.081	17.7 ± 0.478	30.2 ± 0.363	9.52 ± 0.278	0.809 ± 0.17	5.12 ± 0.117
ZSDV-00040	0.049 ± 0.001	2.06 ± 0.021	0.840 ± 0.008	6.44 ± 0.097	2.96 ± 0.018	2.33 ± 0.116	1.07 ± 0.057	0.642 ± 0.028	0.303 ± 0.004
ZSDV-00044	0.022 ± 0.001	1.04 ± 0.010	1.69 ± 0.019	1.76 ± 0.011	3.76 ± 0.079	1.51 ± 0.024	4.84 ± 0.247	0.498 ± 0.017	5.51 ± 0.198
ZSDV-00045	0.507 ± 0.009	0.635 ± 0.013	2.81 ± 0.028	14.8 ± 0.133	3.92 ± 0.030	30.1 ± 0.242	8.78 ± 0.462	0.653 ± 0.004	1.12 ± 0.062
ZSDV-00046	0.084 ± 0.006	0.367 ± 0.006	0.757 ± 0.017	2.54 ± 0.021	2.40 ± 0.019	4.77 ± 0.124	1.46 ± 0.095	0.660 ± 0.009	1.02 ± 0.029
ZSDV-00048	0.237 ± 0.005	0.377 ± 0.003	1.10 ± 0.005	2.30 ± 0.032	1.36 ± 0.015	1.86 ± 0.080	0.810 ± 0.070	0.647 ± 0.019	1.27 ± 0.037
ZSDV-00053	0.132 ± 0.004	6.06 ± 0.036	3.86 ± 0.093	10.2 ± 0.051	55.9 ± 0.615	10.0 ± 0.350	6.93 ± 0.077	1.71 ± 0.031	26.9 ± 0.457
ZSDV-00054	0.820 ± 0.005	3.40 ± 0.058	1.31 ± 0.018	1.4 ± 0.021	7.39 ± 0.059	3.20 ± 0.70	1.17 ± 0.066	0.760 ± 0.005	9.08 ± 0.073
ZSDV-00055	0.369 ± 0.003	0.301 ± 0.005	0.442 ± 0.003	1.40 ± 0.015	1.38 ± 0.035	1.59 ± 0.046	1.27 ± 0.062	0.525 ± 0.011	0.792 ± 0.030
ZSDV-00056	0.064 ± 0.002	0.972 ± 0.009	3.22 ± 0.016	11.9 ± 0.048	18.4 ± 0.220	2.89 ± 0.064	1.855 ± 0.012	0.817 ± 0.018	15.9 ± 0.254
ZSDV-00058	0.010 ± 0.0009	0.402 ± 0.005	0.445 ± 0.014	0.951 ± 0.030	1.65 ± 0.040	1.34 ± 0.026	0.364 ± 0.052	0.543 ± 0.010	11.6 ± 0.093
ZSDV-00059	0.060 ± 0.002	2.15 ± 0.056	0.637 ± 0.005	2.25 ± 0.009	3.07 ± 0.049	2.07 ± 0.085	1.83 ± 0.028	0.635 ± 0.017	1.63 ± 0.024
ZSDV-00060	0.017 ± 0.0002	0.601 ± 0.004	0.563 ± 0.008	1.53 ± 0.01	2.41 ± 0.022	1.92 ± 0.042	0.631 ± 0.052	0.577 ± 0.007	2.47 ± 0.020
ZSDV-00064	0.027 ± 0.002	0.453 ± 0.005	1.26 ± 0.007	2.89 ± 0.038	1.22 ± 0.020	1.86 ± 0.058	0.568 ± 0.084	0.602 ± 0.010	3.50 ± 0.056
ZSDV-00065	0.016 ± 0.0007	0.709 ± 0.011	0.430 ± 0.004	1.63 ± 0.008	2.09 ± 0.013	2.25 ± 0.012	0.862 ± 0.031	0.542 ± 0.010	2.09 ± 0.033
ZSDV-00066	0.014 ± 0.001	0.491 ± 0.010	0.326 ± 0.008	2.0 ± 0.022	1.85 ± 0.022	1.67 ± 0.033	0.592 ± 0.090	0.612 ± 0.009	2.42 ± 0.036
ZSDV-00070	0.079 ± 0.001	0.486 ± 0.009	0.510 ± 0.006	2.33 ± 0.012	1.19 ± 0.033	88.9 ± 0.800	29.3 ± 2.06	0.606 ± 0.008	3.57 ± 0.071
ZSDV-00072	0.054 ± 0.001	0.577 ± 0.005	0.828 ± 0.017	2.70 ± 0.032	2.84 ± 0.037	2.55 ± 0.49	2.04 ± 0.020	0.600 ± 0.013	2.60 ± 0.021
ZSDV-00074	0.039 ± 0.002	0.264 ± 0.004	1.38 ± 0.007	6.95 ± 0.063	1.66 ± 0.010	4.74 ± 0.090	1.05 ± 0.031	0.559 ± 0.010	0.956 ± 0.016
ZSDV-00075	0.201 ± 0.006	2.23 ± 0.031	1.89 ± 0.025	5.51 ± 0.100	18.6 ± 0.316	4.96 ± 0.050	2.90 ± 0.017	0.968 ± 0.011	6.54 ± 0.052
ZSDV-00076	0.100 ± 0.002	0.572 ± 0.013	7.16 ± 0.037	2.11 ± 0.036	1.09 ± 0.017	30.6 ± 0.184	9.95 ± 0.050	0.579 ± 0.012	3.91 ± 0.101
ZSDV-00077	0.029 ± 0.001	1.73 ± 0.035	0.573 ± 0.009	1.95 ± 0.025	15.0 ± 0.120	9.01 ± 0.117	5.77 ± 0.363	0.634 ± 0.013	5.81 ± 0.186
ZSDV-00078	0.020 ± 0.0004	1.80 ± 0.036	0.853 ± 0.020	2.93 ± 0.053	12.2 ± 0.122	5.01 ± 0.050	2.29 ± 0.060	0.811 ± 0.015	5.14 ± 0.046
ZSDV-00081	0.037 ± 0.001	1.51 ± 0.025	0.593 ± 0.014	1.67 ± 0.027	3.76 ± 0.060	1.94 ± 0.089	0.645 ± 0.053	0.619 ± 0.019	4.55 ± 0.041
ZSDV-00082	0.015 ± 0.0007	0.374 ± 0.012	0.433 ± 0.006	1.26 ± 0.024	1.87 ± 0.041	1.50 ± 0.054	3.96 ± 0.206	0.429 ± 0.009	4.41 ± 0.057
ZSDV-00083	0.403 ± 0.006	18.7 ± 0.093	7.01 ± 0.168	22.3 ± 0.133	313 ± 5.0	16.6 ± 0.730	31.6 ± 0.830	4.29 ± 0.077	78.3 ± 2.82
ZSDV-00084	0.276 ± 0.003	4.51 ± 0.158	3.14 ± 0.056	5.54 ± 0.044	206 ± 2.47	3.52 ± 0.035	9.35 ± 0.252	1.77 ± 0.021	26.4 ± 0.580
ZSDV-00085	0.046 ± 0.003	1.26 ± 0.038	0.835 ± 0.004	3.20 ± 0.058	15.2 ± 0.091	2.41 ± 0.161	1.18 ± 0.034	0.714 ± 0.014	5.70 ± 0.074

(*Continued on next page*)

Table 3. (*Continued*)

Sample	Ca mg/kg	K mg/kg	Mg mg/kg	Na mg/kg	Sr mg/kg	Li mg/kg	Mo mg/kg	Sb mg/kg	Bi mg/kg	Be mg/kg
ZSDV-0001	371,708 ± 10,036	12.8 ± 1.20	160 ± 2.56	42.8 ± 2.09	25.5 ± 0.180	0.101 ± 0.004	0.174 ± 0.013	0.097 ± 0.005	0.218 ± 0.016	0.013 ± 0.001
ZSDV-0003	367,819 ± 8827	108 ± 3.24	130 ± 2.86	44.1 ± 1.01	23.7 ± 0.663	2.05 ± 0.039	0.230 ± 0.012	0.130 ± 0.002	0.186 ± 0.003	0.036 ± 0001
ZSDV-0005	356,181 ± 9616	26.1 ± 0.261	178 ± 3.03	25.0 ± 0.625	36.0 ± 0.396	0.344 ± 0.010	0.222 ± 0.010	0.087 ± 0.0008	0.065 ± 0.004	0.035 ± 0.002
ZSDV-0006	371,778 ± 5948	28.9 ± 0.924	3741 ± 71.0	49.4 ± 0.988	26.8 ± 0.241	0.264 ± 0.008	0.087 ± 0.004	0.036 ± 0.001	0.050 ± 0.0004	0.018 ± 0.001
ZSDV-0007	371,023 ± 8533	97.8 ± 1.85	242 ± 3.87	44.0 ± 1.06	45.8 ± 0.140	1.02 ± 0.020	0.155 ± 0.008	0.067 ± 0.003	0.112 ± 0.004	0.039 ± 0.002
ZSDV-0009	363,513 ± 5816	60.9 ± 1.34	105 ± 1.68	61.9 ± 1.86	23.8 ± 0.428	0.506 ± 0.008	0.113 ± 0.007	0.073 ± 0.002	0.085 ± 0.004	0.028 ± 0.001
ZSDV-00010	374,428 ± 4118	15.9 ± 0.238	82.9 ± 1.74	34.8 ± 0.730	29.3 ± 0.322	0.173 ± 0.005	0.083 ± 0.002	0.030 ± 0.001	0.041 ± 0.002	0.016 ± 0.0008
ZSDV-00011	253,648 ± 1521	2831 ± 56.6	2679 ± 56.2	184 ± 4.60	65.2 ± 0.326	20.4 ± 0.530	1.12 ± 0.019	0.564 ± 0.007	1.65 ± 0.012	0.536 ± 0.026
ZSDV-00018	362,718 ± 3264	94.3 ± 4.33	2836 ± 85.0	43.0 ± 1.20	22.1 ± 0.200	0.553 ± 0.014	0.087 ± 0.007	0.048 ± 0.002	0.060 ± 0.0008	0.041 ± 0.003
ZSDV-00039	356,178 ± 10,329	138 ± 6.07	125 ± 3.87	128 ± 4.73	53.7 ± 0.375	0.542 ± 0.022	10.4 ± 0.166	0.037 ± 0.0007	0.076 ± 0.002	0.032 ± 0.0009
ZSDV-00040	372,672 ± 7826	39.5 ± 1.73	112 ± 2.01	42.8 ± 0.941	16.5 ± 0.297	1.36 ± 0.007	0.259 ± 0.020	0.408 ± 0.002	0.916 ± 0.010	0.029 ± 0.001
ZSDV-00044	371,585 ± 2230	49.9 ± 2.39	93.9 ± 3.0	60.4 ± 2.0	13.0 ± 0.143	1.03 ± 0.031	0.171 ± 0.002	9.63 ± 0.087	2.08 ± 0.029	0.029 ± 0.002
ZSDV-00045	365,923 ± 3293	72.5 ± 3.11	206 ± 3.91	56.8 ± 1.31	9.89 ± 0.208	0.614 ± 0.015	11.0 ± 0.055	0.045 ± 0.0009	0.056 ± 0.005	0.038 ± 0.003
ZSDV-00046	364,092 ± 3276	501 ± 10.0	300 ± 11.7	310 ± 11.8	23.4 ± 0.515	0.263 ± 0.015	1.56 ± 0.017	0.279 ± 0.006	0.052 ± 0.004	0.020 ± 0001
ZSDV-00048	356,042 ± 5340	142 ± 5.39	453 ± 9.51	161 ± 4.50	62.5 ± 0.188	0.307 ± 0.005	0.135 ± 0.012	0.043 ± 0.0009	0.051 ± 0.004	0.028 ± 0.001
ZSDV-00053	332,530 ± 7315	770 ± 11.5	667 ± 17.3	72.1 ± 1.15	37.6 ± 0.639	9.87 ± 0.148	0.390 ± 0.009	0.136 ± 0.0007	0.661 ± 0.007	0.239 ± 0.010
ZSDV-00054	346,585 ± 3119	60.4 ± 3.26	497 ± 16.4	52.6 ± 1.36	27.4 ± 0.384	0.490 ± 0.015	0.325 ± 0.007	0.071 ± 0.001	0.073 ± 0.005	0.049 ± 0.002
ZSDV-00055	349,041 ± 3839	18.8 ± 1.80	44.6 ± 0.669	52.6 ± 1.37	14.0 ± 0.07	0.173 ± 0.010	0.078 ± 0.005	0.050 ± 0.001	0.034 ± 0.001	0.020 ± 0.001
ZSDV-00056	360,480 ± 3605	741 ± 16.3	767 ± 10.7	346 ± 9.34	83.5 ± 1.0	0.910 ± 0.019	0.179 ± 0.006	0.068 ± 0.003	0.098 ± 0.002	0.049 ± 0.002
ZSDV-00058	368,289 ± 12,521	49.6 ± 1.73	1348 ± 22.9	59.9 ± 1.20	468 ± 6.55	0.396 ± 0.013	0.164 ± 0.003	0.218 ± 0.014	0.539 ± 0.020	0.020 ± 0.0006
ZSDV-00059	375,087 ± 6001	261 ± 5.74	120 ± 3.24	206 ± 6.18	31.8 ± 0.413	2.23 ± 0.040	0.173 ± 0.004	0.051 ± 0.002	0.305 ± 0.011	0.054 ± 0.003
ZSDV-00060	363,277 ± 3996	36.4 ± 2.33	63.0 ± 1.32	20.9 ± 0.480	28.3 ± 0.141	0.320 ± 0.006	0.144 ± 0.002	0.028 ± 0.001	0.032 ± 0.001	0.023 ± 0.001
ZSDV-00064	362,113 ± 3983	9.78 ± 0.596	105 ± 3.88	55.4 ± 2.71	28.0 ± 0.168	0.159 ± 0.007	0.184 ± 0.013	3.95 ± 0.028	1.80 ± 0.038	0.018 ± 0.0008
ZSDV-00065	354,857 ± 3193	22.0 ± 1.58	53.8 ± 1.23	51.2 ± 1.18	19.4 ± 0.019	0.266 ± 0.003	0.436 ± 0.004	0.050 ± 0.001	0.074 ± 0.004	0.020 ± 0.001
ZSDV-00066	361,338 ± 2890	15.0 ± 0.480	38.7 ± 1.74	35.8 ± 1.32	19.9 ± 0.179	0.341 ± 0.020	0.118 ± 0.010	0.053 ± 0.0006	0.050 ± 0.002	0.017 ± 0.001
ZSDV-00070	332,894 ± 6324	5.30 ± 0.365	69.3 ± 2.07	38.9 ± 0.933	73.4 ± 0.293	0.131 ± 0.005	32.9 ± 0.395	1.65 ± 0.021	0.183 ± 0.010	0.023 ± 0.001
ZSDV-00072	346,398 ± 6927	20.6 ± 1.42	86.8 ± 3.65	31.1 ± 1.49	18.8 ± 0.075	0.396 ± 0.003	0.471 ± 0.036	0.035 ± 0.001	0.067 ± 0.004	0.024 ± 0.002
ZSDV-00074	349,696 ± 4895	11.0 ± 0.920	310 ± 12.1	26.2 ± 0.681	20.5 ± 0.085	0.146 ± 0.005	0.790 ± 0.011	0.029 ± 0.0006	0.031 ± 0.0007	0.009 ± 0.0007
ZSDV-00075	340,738 ± 2044	1412 ± 53.6	1174 ± 52.8	624 ± 20.0	26.5 ± 0.450	2.21 ± 0.069	0.788 ± 0.017	0.334 ± 0.010	0.227 ± 0.005	0.087 ± 0.003
ZSDV-00076	350,971 ± 8744	11.2 ± 0.638	54.8 ± 1.26	38.4 ± 1.46	22.5 ± 0.428	0.492 ± 0020	11.3 ± 0.158	0.096 ± 0.0006	0.292 ± 0.006	0.023 ± 0.002
ZSDV-00077	362,727 ± 3627	125 ± 3.25	165 ± 4.29	64.4 ± 1.29	22.5 ± 0.225	2.17 ± 0.026	2.68 ± 0.021	3.61 ± 0.029	0.096 ± 0.0008	0.041 ± 0.003
ZSDV-00078	349,736 ± 4896	629 ± 15.7	181 ± 2.90	217 ± 4.12	18.4 ± 0.294	1.83 ± 0.059	1.06 ± 0.010	0.047 ± 0.001	0.181 ± 0.002	0.043 ± 0.004
ZSDV-00081	386,002 ± 3088	76.4 ± 1.98	153 ± 4.74	44.1 ± 0.926	32.3 ± 0.320	1.17 ± 0.043	0.163 ± 0.003	0.119 ± 0.004	0.165 ± 0.006	0.027 ± 0.001
ZSDV-00082	381,863 ± 5727	36.0 ± 3.2	39.6 ± 1.94	103 ± 5.35	21.9 ± 0.153	0.354 ± 0.005	0.139 ± 0.009	5.84 ± 0.058	0.030 ± 0.0009	0.008 ± 0.0008
ZSDV-00083	258,198 ± 6196	1917 ± 47.9	1972 ± 90.7	253 ± 9.36	65.6 ± 0.721	20.4 ± 0.653	0.859 ± 0.015	9.36 ± 0.225	0.997 ± 0.017	0.719 ± 0.029
ZSDV-00084	344,682 ± 3102	374 ± 10.8	662 ± 22.5	101 ± 8.48	77.2 ± 0.463	3.69 ± 0.130	0.287 ± 0.010	6.52 ± 0.085	0.226 ± 0.012	0.183 ± 0.016
ZSDV-00085	351,033 ± 9477	163 ± 6.84	154 ± 4.0	51.6 ± 1.90	30.2 ± 0.513	0.736 ± 0.026	0.117 ± 0.010	0.051 ± 0.0003	0.071 ± 0.003	0.044 ± 0.004

ZSDV-0001	63.1 ± 0.640	0.035 ± 0.0006	0.204 ± 0.006	11.2 ± 0.347	50.7 ± 1.36	3.75 ± 0.064	0.347 ± 0.007	132 ± 2.38	122 ± 4.74	2.33 ± 0.075	0.161 ± 0.020
ZSDV-0003	328 ± 2.01	1.87 ± 0.020	1.20 ± 0.012	15.0 ± 0.345	676 ± 10.8	21.3 ± 0.213	0.299 ± 0.006	460 ± 9.57	183 ± 1.83	1.10 ± 0.031	1.35 ± 0.025
ZSDV-0005	209 ± 5.43	0.026 ± 0.0006	0.309 ± 0.002	8.88 ± 0.390	324 ± 6.15	11.2 ± 0.120	0.181 ± 0.005	348 ± 2.78	136 ± 3.26	0.804 ± 0.030	0.203 ± 0.081
ZSDV-0006	153 ± 2.30	0.010 ± 0.0003	0.318 ± 0.010	10.0 ± 0.400	218 ± 3.48	13.6 ± 0.108	0.141 ± 0.003	292 ± 4.08	117 ± 2.46	2.59 ± 0.052	0.105 ± 0.019
ZSDV-0007	1084 ± 19.5	0.044 ± 0.001	0.401 ± 0.005	12.1 ± 0.278	941 ± 22.6	41.5 ± 0.954	0.186 ± 0.003	1022 ± 7.15	155 ± 3.10	1.18 ± 0.033	0.392 ± 0.013
ZSDV-0009	328 ± 8.20	0.043 ± 0.001	0.120 ± 0.001	8.61 ± 0.250	499 ± 15.0	23.2 ± 1.11	0.120 ± 0.004	531 ± 14.3	115 ± 2.77	0.853 ± 0.070	0.243 ± 0.010
ZSDV-00010	86.5 ± 2.33	0.006 ± 0.0002	0.329 ± 0.006	10.5 ± 0.325	87.4 ± 0.620	5.82 ± 0.110	0.126 ± 0.002	191 ± 3.25	151 ± 1.36	2.71 ± 0.019	0.292 ± 0.039
ZSDV-00011	12,040 ± 409	0.959 ± 0.024	2.26 ± 0.032	24.3 ± 0.996	7581 ± 257	723 ± 18.0	0.569 ± 0.010	14,977 ± 284	187 ± 4.30	3.91 ± 0.090	4.92 ± 0.0146
ZSDV-00018	304 ± 6.68	0.019 ± 0.0007	0.454 ± 0.009	13.6 ± 0.476	596 ± 5.36	22.0 ± 0.308	0.128 ± 0.003	525 ± 6.82	140 ± 1.96	2.81 ± 0.067	0.240 ± 0.037
ZSDV-00039	419 ± 8.80	0.027 ± 0.0006	0.448 ± 0.009	17.3 ± 0.536	799 ± 20.7	29.8 ± 0.271	0.222 ± 0.006	760 ± 12.1	144 ± 1.87	2.80 ± 0.037	0.224 ± 0.037
ZSDV-00040	361 ± 6.86	0.086 ± 0.002	0.167 ± 0.017	10.1 ± 0.272	430 ± 5.59	14.4 ± 0.460	0.101 ± 0.005	457 ± 7.77	135 ± 3.62	1.09 ± 0.018	0.307 ± 0.088
ZSDV-00044	600 ± 12.0	0.108 ± 0.001	0.105 ± 0.002	2.18 ± 0.090	574 ± 9.18	29.7 ± 0.475	0.132 ± 0.004	254 ± 4.07	152 ± 3.04	1.88 ± 0.042	1.21 ± 0.085
ZSDV-00045	380 ± 6.08	0.023 ± 0.0004	0.303 ± 0.005	10.5 ± 0.231	640 ± 14.7	24.4 ± 0.488	0.118 ± 0.002	452 ± 7.23	114 ± 2.73	0.759 ± 0.010	0.128 ± 0.029
ZSDV-00046	159 ± 3.34	0.014 ± 0.0006	0.300 ± 0.003	8.40 ± 0.353	148 ± 8.28	8.65 ± 0.198	0.100 ± 0.002	293 ± 1.76	173 ± 2.25	1.11 ± 0.023	0.175 ± 0.049
ZSDV-00048	163 ± 5.22	0.009 ± 0.0006	0.604 ± 0.009	12.5 ± 0.512	230 ± 9.66	8.18 ± 0.171	0.102 ± 0.003	272 ± 1.63	198 ± 3.36	1.13 ± 0.040	0.09 ± 0.001
ZSDV-00053	4644 ± 195	0.670 ± 0.013	1.38 ± 0.028	20.0 ± 0.620	5278 ± 132	206 ± 11.9	0.238 ± 0.005	4440 ± 44.4	152 ± 2.28	1.70 ± 0.042	3.20 ± 0.057
ZSDV-00054	301 ± 8.43	0.043 ± 0.0006	0.407 ± 0.008	10.1 ± 0.363	420 ± 9.66	22.2 ± 0.310	0.093 ± 0.007	481 ± 5.28	155 ± 2.18	1.09 ± 0.028	0.484 ± 0.024
ZSDV-00055	100 ± 2.50	0.004 ± 0.0002	0.307 ± 0.005	11.1 ± 0.421	129 ± 6.96	9.80 ± 0.362	0.072 ± 0.002	211 ± 1.30	151 ± 2.86	2.80 ± 0.065	0.208 ± 0.054
ZSDV-00056	1264 ± 40.4	0.050 ± 0.0006	0.872 ± 0.013	8.55 ± 0.316	1687 ± 40.5	42.3 ± 1.18	0.095 ± 0.004	1041 ± 4.16	135 ± 1.08	0.885 ± 0.037	0.448 ± 0.015
ZSDV-00058	191 ± 3.44	0.019 ± 0.0006	0.964 ± 0.021	11.3 ± 0.452	195 ± 4.48	3.34 ± 0.097	0.255 ± 0.018	151 ± 1.81	101 ± 1.62	2.79 ± 0.017	0.190 ± 0.011
ZSDV-00059	1456 ± 59.7	0.027 ± 0.0002	0.237 ± 0.005	141 ± 4.79	433 ± 15.1	15.5 ± 0.480	0.065 ± 0.004	506 ± 3.54	124 ± 0.865	2.49 ± 0.045	0.877 ± 0.061
ZSDV-00060	197 ± 6.50	0.018 ± 0.0004	0.869 ± 0.013	7.63 ± 0.267	307 ± 5.83	10.4 ± 0.083	0.051 ± 0.0006	330 ± 0.700	100 ± 2.03	0.565 ± 0.025	0.212 ± 0.033
ZSDV-00064	96.8 ± 4.45	<0.003	0.230 ± 0.003	14.0 ± 0.476	61.0 ± 1.58	3.35 ± 0.064	0.075 ± 0.004	193 ± 2.31	195 ± 3.11	0.987 ± 0.019	0.206 ± 0.011
ZSDV-00065	240 ± 6.48	0.004 ± 0.0003	0.281 ± 0.010	40.2 ± 1.85	97.2 ± 6.02	4.82 ± 0.212	0.056 ± 0.001	210 ± 1.26	145 ± 2.47	2.55 ± 0.064	0.302 ± 0.012
ZSDV-00066	144 ± 4.90	0.013 ± 0.0007	0.106 ± 0.002	11.3 ± 0.350	143 ± 4.57	7.31 ± 0.285	0.063 ± 0.002	262 ± 2.36	159 ± 1.91	0.856 ± 0.012	0.534 ± 0.032
ZSDV-00070	97.8 ± 3.81	<0.003	0.505 ± 0.017	12.8 ± 0.550	38.8 ± 1.04	2.25 ± 0.065	0.158 ± 0.002	188 ± 2.83	188 ± 5.25	0.958 ± 0.043	0.121 ± 0.007
ZSDV-00072	259 ± 10.6	0.027 ± 0.001	0.358 ± 0.009	12.0 ± 0.456	301 ± 2.70	12.2 ± 0.146	0.077 ± 0.002	403 ± 7.65	178 ± 4.26	1.0 ± 0.32	0.265 ± 0.012
ZSDV-00074	74.5 ± 2.16	0.022 ± 0.0007	0.276 ± 0.004	10.1 ± 0.393	103 ± 3.29	2.53 ± 0.071	0.046 ± 0.0004	150 ± 1.80	123 ± 3.57	0.831 ± 0.010	0.139 ± 0.001
ZSDV-00075	2176 ± 69.6	0.226 ± 0.005	0.698 ± 0.011	13.2 ± 0.871	2207 ± 59.5	68.6 ± 1.92	0.129 ± 0.004	2094 ± 18.9	197 ± 3.75	1.54 ± 0.041	1.19 ± 0.010
ZSDV-00076	126 ± 4.28	0.027 ± 0.0004	0.258 ± 0.006	14.1 ± 0.451	143 ± 1.72	7.18 ± 0.603	0.090 ± 0.001	217 ± 1.2	169 ± 1.52	1.0 ± 0.034	0.140 ± 0.001
ZSDV-00077	923 ± 24.0	0.053 ± 0.001	0.130 ± 0.003	0.831 ± 0.056	1116 ± 21.2	29.6 ± 0.266	0.053 ± 0.001	448 ± 8.07	77.5 ± 1.47	0.959 ± 0.026	1.07 ± 0.050
ZSDV-00078	497 ± 20.8	0.376 ± 0.006	0.426 ± 0.010	7.67 ± 0.268	1012 ± 17.2	107 ± 1.61	0.294 ± 0.003	1128 ± 13.5	129 ± 3.10	0.933 ± 0.025	1.10 ± 0.065
ZSDV-00081	344 ± 5.50	0.106 ± 0.004	0.192 ± 0.004	14.6 ± 0.495	552 ± 5.52	19.7 ± 0.354	0.278 ± 0.020	359 ± 5.39	141 ± 2.26	3.23 ± 0.058	0.515 ± 0.025
ZSDV-00082	118 ± 3.54	0.004 ± 0.0001	0.065 ± 0.001	0.417 ± 0.018	89.4 ± 2.59	3.26 ± 0.101	0.046 ± 0.002	89.5 ± 2.15	115 ± 2.40	1.39 ± 0.030	0.364 ± 0.015
ZSDV-00083	17,263 ± 915	0.333 ± 0.008	1.50 ± 0.024	11.0 ± 0.396	8716 ± 357	571 ± 14.8	0.418 ± 0.008	9378 ± 206	228 ± 3.75	4.77 ± 0.085	5.03 ± 0.246
ZSDV-00084	4424 ± 150	0.112 ± 0.002	0.322 ± 0.005	1.63 ± 0.092	2843 ± 59.7	78.4 ± 1.25	0.121 ± 0.003	1814 ± 54.8	178 ± 4.45	2.52 ± 0.060	0.801 ± 0.032
ZSDV-00085	511 ± 15.8	0.022 ± 0.0002	1.0 ± 0.037	10.7 ± 0.353	925 ± 24.9	31.9 ± 0.510	0.081 ± 0.004	840 ± 12.6	163 ± 3.76	1.02 ± 0.034	0.451 ± 0.016

a few square meters large and mostly up to 20 cm deep), the second source is mostly certain rock weathering. In the sample from Mandića cave (ZSDV-0039) quartz was detected besides calcite. The possible source of Si is influshed, fine-grained clastic sediment (Lovrenčić Mikelić et al., 2013). In two samples, one from Zagorska peć (ZSDV-0054) and one from Vrelo (ZSDV-0075), dolomite was detected besides calcite. It is a reflection of the local geological conditions, e.g. occurrence of dolomite and dolomitic limestone (Bahun, 1970; Garašić, 1992).

3.2. ICP-MS analysis of trace elements and statistical interpretation

Results of ICP-MS analysis of 30 chemical elements are presented in Table 3 and their basic statistical parameters are presented in Table 4. Parameters are obtained for all 30 analyzed elements, including all samples from all studied caves to get a brief insight into the concentration ranges of studied elements in the studied caves that belong to Croatian karst. These values could serve as reference values for the mentioned region and could be compared with values of some other karst regions worldwide.

Results of the correlation analysis of log-transformed data between 30 elements are given in Table 5. The majority of the element mass fractions were strongly correlated with each other (Table 6). There are a total of 71 cases (16.3%) of strong relationships, 171 cases (39.3%) of moderate strong relationships, and 106 cases (24.4%) of weak relationships. Strong and moderate strong positive relationships dominate over strong and moderate strong negative relationships (9.1:1). Their prevalence indicates influence of similar sources. Due to the prevalence of calcite, the most abundant element is Ca. It is expected due to the carbonate host rocks and Ca high solubility and mobility. It has negative correlations with all other elements. Similar relationships of Ca with other elements were identified in carbonate rocks by Lovrenčić Mikelić et al. (2013) so there are similarities between host rock and speleothem composition.

Results of boxplot evaluation of anomalies, which are according to their intensity divided into extremes and outliers, are presented in Table 7. The largest number of anomalies is present in all three samples from Lukina jama (ZSDV-0011, ZSDV-0053, ZSDV-0083) located on Northern Velebit Mt. In this cave a whole series of elements, including many heavy metals, show extreme values (Pb, Cu, Zn, Mn, Ni, Cr, Co, Ba, K, Mg, Li, Be, Al, U, Si, Ti, W, Fe, As). Among all samples, all three samples from Lukina jama show the highest anomalies of Fe and Mn. According to previous research it is probably an effect of Mn—Fe crusts showing changes of hydrological conditions (Gázquez et al., 2011). It is also known that other types of mineral coatings affect speleothem mineralogy (Onac, 1996). The other location with a larger number of anomalies, but to a much lower extent than Lukina jama, is cave Špilja u kamenolomu Tounj (ZSDV-0084), where Pb, Mn, Co, Sb, Be and Al show extreme values and Ba, Sr, Li, Si, Ti and Fe outlier values. Mandića špilja (ZSDV-0039) has extreme values of Cu, Zn, Ni and Mo. Fabrisova jama (ZSDV-0070) also shows four extremes (Ni, Cr, Mo, Sb) and one outlier (Sr). Vrelo cave (ZSDV-0075) shows three extremes (K, Na, Al) and four outliers (Mg, Si, Ti, Fe). It is interesting that in its clastic sediment abundant hematite particles were found (Garašić, 1992). We found increased concentration of Fe in speleothem too but not so high since Fe in clastic sediment is a part of alluvial deposit from a different source and reflects geological influence from a wider drainage aquifer system. Meduza cave (ZSDV-0076) shows three extremes (Cu, Ni, Mo). The sample from Sedrena špilja iza mlina (ZSDV-0058) has the highest concentration of Sr. It is a cave formed in tufa deposits. Sr is known to be incorporated in larger quantities at high growth rates that are due to the high porosity of tufa and precipitation but it can also reflect change in water chemistry due to the *prior calcite precipitation*, aeolian input, Sr-bearing salts that were precipitated in drying soils in the summer and summer dryness in general (Lorens, 1981; Fairchild et al., 2000; Ihlenfeld et al., 2003; Fairchild and Treble, 2009). So it would be interesting to collect more samples of speleothems from other tufa caves for comparison because of less complicated sampling and not so complicated geological conditions that can be also analyzed for determination of precipitation environment and controls. All other caves show a much lower number of anomalies, which are not so important, or do not show any anomaly at all.

Table 4
Basic statistical parameters of mass fractions. Values are given in mg/kg.

	Valid N	Mean	Median	Minimum	Maximum	Variance	Std.Dev.	Std. Error	Skewness	Kurtosis
Cd	37	0.1	0.1	0.0	0.8	0	0.18	0.030	2.04910	4.30203
Pb	37	2.4	1.0	0.2	18.7	19	4.34	0.714	2.89760	7.75418
Cu	37	1.9	0.9	0.3	9.9	6	2.45	0.403	2.27051	4.41621
Zn	37	5.5	2.7	1.0	26.9	45	6.71	1.103	2.31994	4.76560
Mn	37	27.9	3.1	1.1	313.0	5063	71.15	11.698	3.27011	9.89031
Ni	37	8.7	2.5	1.3	88.9	265	16.28	2.676	3.75306	16.52799
Cr	37	4.6	1.5	0.4	31.6	54	7.35	1.208	2.72483	7.37915
Co	37	0.9	0.6	0.4	5.1	1	0.96	0.157	3.68208	13.49132
Ba	37	10.0	4.1	0.3	80.9	323	17.97	2.954	3.41012	11.59468
Ca	37	354,266.0	361,338.0	253,648.0	386,002.0	721,965,777	26,869.42	4417.306	−2.75712	8.74052
K	37	296.8	60.9	5.3	2831.0	348,958	590.73	97.115	3.09392	10.18039
Mg	37	545.1	160.0	38.7	3741.0	772,335	878.83	144.478	2.42447	5.43810
Na	37	103.6	52.6	20.9	624.0	14,391	119.96	19.722	2.80522	9.37908
Sr	37	45.0	26.8	9.9	468.0	5475	73.99	12.164	5.47236	31.80590
Li	37	2.1	0.5	0.1	20.4	22	4.74	0.779	3.46038	11.50241
Mo	37	2.1	0.2	0.1	32.9	36	5.97	0.982	4.26118	20.28691
Sb	37	1.2	0.1	0.0	9.6	7	2.57	0.422	2.42829	5.02851
Bi	37	0.3	0.1	0.0	2.1	0	0.52	0.085	2.39947	5.06241
Be	37	0.1	0.0	0.0	0.7	0	0.14	0.024	3.71974	14.02126
Al	37	1408.8	304.0	63.1	17,263.0	11,761,366	3429.48	563.804	3.78724	14.81245
Tl	37	0.1	0.0	0.0	1.9	0	0.35	0.058	3.91534	16.95588
U	37	0.5	0.3	0.1	2.3	0	0.47	0.077	2.03934	4.70345
B	37	15.1	11.1	0.4	141.0	498	22.31	3.668	5.28168	30.06720
Si	37	1097.0	430.0	38.8	8716.0	3,900,600	1974.99	324.687	2.96788	8.52927
Ti	37	60.5	15.5	2.3	723.0	21,933	148.10	24.347	3.82993	14.54889
W	37	0.2	0.1	0.0	0.6	0	0.12	0.019	1.82545	3.73879
Fe	37	1240.5	403.0	89.5	14,977.0	8,068,781	2840.56	466.985	4.02453	16.95595
V	37	149.3	151.0	77.5	228.0	1050	32.40	5.326	0.16463	−0.10955
Sn	37	1.7	1.1	0.6	4.8	1	1.02	0.167	1.10868	0.70681
As	37	0.8	0.3	0.1	5.0	1	1.17	0.193	2.94461	8.41506

Table 5
Correlation coefficients of log-transformed data for 30 elements. Elevation (z) and precipitation (P). Correlations are significant at $p < 0.05$.

	Al	As	B	Ba	Be	Bi	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn
Al	1.00															
As	0.84	1.00														
B	0.07	−0.01	1.00													
Ba	0.67	0.67	−0.08	1.00												
Be	0.94	0.79	0.16	0.71	1.00											
Bi	0.51	0.55	0.15	0.41	0.52	1.00										
Ca	−0.65	−0.58	−0.17	−0.59	−0.78	−0.41	1.00									
Cd	0.45	0.19	0.17	0.21	0.60	0.05	−0.52	1.00								
Co	0.83	0.67	0.13	0.71	0.91	0.45	−0.86	0.52	1.00							
Cr	0.58	0.47	−0.15	0.45	0.60	0.33	−0.61	0.47	0.55	1.00						
Cu	0.63	0.38	0.11	0.50	0.67	0.41	−0.59	0.62	0.66	0.65	1.00					
Fe	0.93	0.78	0.18	0.67	0.95	0.43	−0.76	0.55	0.91	0.55	0.69	1.00				
K	0.85	0.71	0.06	0.57	0.80	0.31	−0.52	0.42	0.70	0.40	0.53	0.85	1.00			
Li	0.95	0.89	0.04	0.65	0.90	0.56	−0.61	0.38	0.78	0.57	0.58	0.89	0.83	1.00		
Mg	0.53	0.29	0.11	0.62	0.58	0.24	−0.45	0.37	0.63	0.13	0.41	0.57	0.60	0.46	1.00	
Mn	0.92	0.73	−0.08	0.74	0.89	0.34	−0.66	0.47	0.87	0.55	0.66	0.92	0.80	0.84	0.59	1.00
Mo	0.10	−0.03	0.03	0.00	0.15	0.11	−0.30	0.30	0.13	0.70	0.44	0.14	0.05	0.10	−0.07	0.08
Na	0.56	0.43	0.05	0.32	0.48	0.24	−0.35	0.28	0.43	0.34	0.39	0.52	0.80	0.49	0.42	0.48
Ni	0.33	0.18	0.11	0.25	0.43	0.21	−0.55	0.48	0.43	0.84	0.62	0.42	0.23	0.33	0.10	0.34
Pb	0.83	0.74	0.09	0.59	0.83	0.47	−0.58	0.44	0.71	0.47	0.56	0.82	0.68	0.84	0.41	0.82
Sb	0.36	0.42	−0.55	0.36	0.32	0.58	−0.30	0.01	0.29	0.50	0.17	0.18	0.18	0.36	0.07	0.31
Si	0.94	0.78	0.00	0.65	0.89	0.38	−0.56	0.49	0.76	0.49	0.65	0.93	0.87	0.92	0.57	0.91
Sn	0.36	0.34	0.21	0.47	0.38	0.32	−0.34	0.12	0.45	0.17	0.18	0.30	0.28	0.33	0.41	0.36
Sr	0.28	0.08	0.10	0.49	0.31	0.26	−0.28	0.05	0.35	0.08	0.18	0.24	0.27	0.19	0.46	0.29
Ti	0.92	0.81	0.05	0.66	0.91	0.41	−0.65	0.51	0.83	0.53	0.66	0.96	0.86	0.91	0.53	0.92
Tl	0.71	0.78	0.05	0.55	0.69	0.50	−0.42	0.28	0.58	0.37	0.49	0.73	0.69	0.83	0.40	0.65
U	0.49	0.36	0.41	0.56	0.62	0.22	−0.61	0.38	0.59	0.25	0.42	0.63	0.54	0.46	0.57	0.47
V	0.26	0.25	0.30	0.25	0.40	0.32	−0.50	0.44	0.41	0.32	0.37	0.37	0.23	0.22	0.13	0.22
W	0.43	0.42	0.23	0.57	0.53	0.50	−0.46	0.27	0.58	0.30	0.39	0.53	0.43	0.48	0.48	0.46
Zn	0.63	0.38	0.19	0.38	0.63	0.28	−0.57	0.53	0.67	0.55	0.80	0.73	0.57	0.56	0.44	0.69
z	0.41	0.65	−0.14	0.29	0.33	0.31	−0.26	−0.09	0.28	0.42	0.08	0.35	0.34	0.58	−0.11	0.29
p	0.38	0.62	−0.16	0.23	0.29	0.40	−0.21	−0.09	0.22	0.30	0.04	0.30	0.34	0.50	−0.08	0.23

	Mo	Na	Ni	Pb	Sb	Si	Sn	Sr	Ti	Tl	U	V	W	Zn	z	p
Mo	1.00															
Na	0.15	1.00														
Ni	0.91	0.19	1.00													
Pb	0.04	0.38	0.28	1.00												
Sb	0.16	0.26	0.17	0.29	1.00											
Si	0.06	0.49	0.29	0.81	0.20	1.00										
Sn	−0.16	0.26	−0.03	0.27	0.19	0.25	1.00									
Sr	0.00	0.24	0.12	0.14	0.16	0.20	0.31	1.00								
Ti	0.08	0.51	0.34	0.82	0.20	0.96	0.31	0.11	1.00							
Tl	0.07	0.33	0.25	0.68	0.15	0.80	0.15	0.07	0.79	1.00						
U	0.11	0.28	0.34	0.33	−0.15	0.53	0.20	0.52	0.52	0.45	1.00					
V	0.10	0.29	0.24	0.20	0.20	0.17	0.20	0.10	0.26	0.17	0.38	1.00				
W	0.12	0.23	0.32	0.40	0.10	0.46	0.48	0.40	0.54	0.63	0.51	0.29	1.00			
Zn	0.36	0.39	0.57	0.55	0.06	0.66	0.16	0.11	0.66	0.50	0.44	0.27	0.43	1.00		
z	0.17	0.21	0.24	0.40	0.30	0.37	0.09	−0.14	0.43	0.57	−0.02	0.06	0.24	−0.02	1.00	
p	0.09	0.35	0.09	0.37	0.42	0.30	0.05	−0.06	0.34	0.51	−0.09	0.24	0.14	−0.09	0.86	1.00

$0 < |r| < 0.20$ = not or slightly correlated; $0.20 \le |r| < 0.40$ = weak linear relationship;
$0.40 \le |r| < 0.70$ = moderate strong linear relationship; $0.70 \le |r| < 1$ = strong linear relationship.

Results of Q-mode cluster analysis are presented in Table 8 (members of each of three extracted clusters and Euclidean distances from respective cluster center) and Table 9 (mean values of elements for all three clusters). Cluster analysis was performed using 10 selected elements (Pb, Zn, Ni, Cr, Co, Ca, Li, Al, Si and Fe) and 2 other variables (elevation and precipitation). Cluster 1 contains 15 samples and cluster 3 contains 20 locations. Differences of mean values of most elements between them are not very big, while cluster 2, which contains only two samples from Lukina jama, has significantly increased values of almost all elements and parameters. Those two samples are so much different than any other sample, that they formed their own cluster.

To get an even better insight into the behavior of factors of studied speleothems, factor statistical analysis was performed. The results of factor analyses are presented in Table 10 (factor loadings) and in Table 11 (factor scores for each studied sample). Three factors (varimax normalized) were extracted, and the obtained results fit well with the stipulation of Morrison (1967) that main components should explain at least 75% of the total variance (in our dataset 89.36% of the total variance is explained with three factors). In the obtained factor model 10 chemical elements were included and 2 other variables (elevation above sea level of the cave entrance and precipitation).

Factor 1 has very good or excellent positive correlations with the following chemical elements: Pb, Zn, Co, Li, Al, Si and Fe, while with Ca it has very good negative correlation. So, it can be concluded that this factor is obviously a natural factor caused by local mineralogy, influenced by aluminosilicate rocks. The highest factor scores of this factor are present in samples from Lukina jama cave, in which the largest number of mineral phases was detected. Factor scores of this factor are also rather high in caves Špilja u kamenolomu Tounj, Maklutača, Gvozdenica and Mandića Špilja. The majority of these caves have complex mineralogical composition.

Factor 2 has excellent positive correlations with elevation of cave entrance (e.g. surface drainage area) and with precipitation. The highest factor scores are present in several caves located on Velebit Mt. and in

Table 6
Distribution of correlation relationship strength.

r value	Relationship strength	Cases N	Cases %
$-1 < r \leq -0.7$	Strong negative linear relationship	3	0.7
$-0.7 < r \leq -0.4$	Moderate strong negative linear relationship	21	4.8
$-0.4 < r \leq -0.2$	Weak negative linear relationship	5	1.1
$-0.2 < r \leq 0$	Not or slightly correlated	11	2.5
$0 < r < 0.2$	Not or slightly correlated	76	17.5
$0.2 \leq r < 0.4$	Weak positive linear relationship	101	23.2
$0.4 \leq r < 0.7$	Moderate strong positive linear relationship	150	34.5
$0.7 \leq r < 1$	Strong positive linear relationship	68	15.6

Class thresholds for *r* value taken from Lovrenčić Mikelić et al., 2013.

Gorski kotar region. Those caves are mostly located at high elevations (>1200 m) and/or have the highest rate of precipitation (~2000 mm/y; the amount is not connected only with the elevation but also with the geographical position near the Adriatic Sea as the source of humid air masses and influences from the Atlantic; Table 1). It is an expected result but it is stressed here because of the impact on the transport of mineral phases between the surface and the underground, e.g. weathering and accumulation environments. Vadose circulation (diffuse and concentrated), underground flash floods after snow melting or heavy rains, together with allogenic streams can transport remarkable amounts of inorganic and organic matter and energy through conduits influencing both weathering and accumulation in cave sediments, including speleothems. Therefore the correlation between elevation/precipitation and elemental composition is also interesting (Table 12). Due to the interconnections of surface and cave microclimate increase in elevation (z) can be observed as the factor influencing air/water temperature oscillations and thus speleothem deposition and composition (Domínguez-Villar et al., 2013; Paar et al., 2013a; Rau et al., 2015). Statistical analysis indicates the highest values of positive correlation between precipitation and concentrations of As, Na and K. Carbonates are normally low in As, usually around 1 mg/kg or less (Onishi and Sandell, 1955; Salminen et al., 2005; Lovrenčić Mikelić et al., 2013), so our results are consistent with literature data. In sedimentary rocks, As is concentrated in clays and hydrous Fe and Mn oxides. In our case it is confirmed by strong correlation with Fe and Mn ($r = 0.78$ and 0.73) but also with Al and Si (0.84 and 0.78) as compounds of clay minerals, e.g. secondary aluminosilicates found in our examples (Tables 3 and 5). As minerals and compounds are readily soluble, but As migration is greatly limited, because of strong sorption by clays, hydroxides and organic matter; the latter may have a marked influence on the

Table 7
Anomalies (extremes and outliers) determined by boxplot method. Elements V and Sn did not show any anomalous values, all other showed some anomalies.

Location	Anomaly of following element: Extreme	Outlier
ZSDV-0001		
ZSDV-0003	Tl	U
ZSDV-0005		
ZSDV-0006	Mg	
ZSDV-0007		
ZSDV-0009	Pb	
ZSDV-00010		
ZSDV-00011	Al, As, Ba, Be, Bi, Ca(−), Co, Cr, Cu, Fe, K, Li, Mg, Mn, Ni, Pb, Si, Ti, U, W, Zn	B, Cd, Sr
ZSDV-00018	Mg	
ZSDV-00039	Cu, Mo, Ni, Zn	
ZSDV-00040	Bi	
ZSDV-00044	Bi, Sb	
ZSDV-00045	Mo, Ni	Cd, Zn
ZSDV-00046	Na	K
ZSDV-00048		Sr
ZSDV-00053	Al, As, Be, Co, Fe, K, Li, Mn, Si, Ti	Ba, Bi, Cu, Ni, Pb, U
ZSDV-00054	Cd	
ZSDV-00055		
ZSDV-00056	K, Na	Sr, Zn
ZSDV-00058	Sr	Bi, Mg
ZSDV-00059	B	Al, Na
ZSDV-00060		
ZSDV-00064	Bi, Sb	
ZSDV-00065	B	
ZSDV-00066		
ZSDV-00070	Cr, Mo, Ni, Sb	Sr
ZSDV-00072		
ZSDV-00074		
ZSDV-00075	Al, K, Na	Fe, Mg, Si, Ti
ZSDV-00076	Cu, Mo, Ni	
ZSDV-00077	Sb	Mo
ZSDV-00078	K, Ti	Na
ZSDV-00081		
ZSDV-00082	Sb	
ZSDV-00083	Al, As, Ba, Be, Bi, Ca(−), Co, Cr, Cu, Fe, K, Li, Mg, Mn, Sb, Si, Ti, Zn	Na, Sr, U, W
ZSDV-00084	Al, Be, Co, Mn, Pb, Sb	Ba, Fe, Li, Sr, Si, Ti
ZSDV-00085		

(−) negative anomaly.

Table 8
Members of obtained clusters and distances from respective cluster centers.

Members of cluster number 1 and distances from respective cluster center. cluster contains 15 cases.	Distance
ZSDV-0005, špilja rudnik Minjera, Brač	2435.738
ZSDV-00039, Mandića špilja, Omiš	2419.325
ZSDV-00048, Jama Povajska Lipotica, Brač	2403.728
ZSDV-00053, Lukina jama, Sjev. Velebit	4829.115
ZSDV-00054, Zagorska peć, Ogulin	463.633
ZSDV-00055, Provala, Žumberak	551.427
ZSDV-00065, Špilja Barići, Kremen-Slunj	2065.512
ZSDV-00070, Fabrisova jama, Ročko polje, Istra	4334.853
ZSDV-00072, Pčelina špilja, Gospić	527.825
ZSDV-00074, Kraljevska jama, Hvar	708.462
ZSDV-00075, Vrelo, Fužine	2169.458
ZSDV-00076, Meduza, Sjev. Velebit	1036.864
ZSDV-00078, Velebita, Sjev. Velebit	645.387
ZSDV-00084, Špilja u kamenolomu Tounj	1483.106
ZSDV-00085, Veternica, Medvednica	942.042
Members of cluster number 2 and distances from respective cluster center. cluster contains 2 cases.	**Distance**
ZSDV-00011, Lukina jama, Sjev. Velebit	1295.985
ZSDV-00083, Lukina jama, Sjev. Velebit	1295.985
Members of cluster number 3 and distances from respective cluster center. cluster contains 20 cases.	**Distance**
ZSDV-0001, Jopićeva špilja, Kordun	837.307
ZSDV-0003, Lubuška jama, Sjev. Velebit	429.977
ZSDV-0006, Dolača, Žumberak	839.202
ZSDV-0007, Golubnjača, Plitvice	676.251
ZSDV-0009, Maklutača, Dugopolje	1563.365
ZSDV-00010, Provala, Žumberak	1605.004
ZSDV-00018, Markova špilja, Hvar	1810.684
ZSDV-00040, Manita Peć, N.P. Paklenica	1089.603
ZSDV-00044, Munižaba, Crnopac	809.341
ZSDV-00045, Rača špilja, Lastovo	909.087
ZSDV-00046, Vodarica, N.P. Paklenica	1405.155
ZSDV-00056, Gvozdenica, Kordun	2484.982
ZSDV-00058, Sedrena špilja, Krka	268.197
ZSDV-00059, Debeljača, Lovinac	1805.601
ZSDV-00060, Nova Grgosova špilja, Otruševac	1637.695
ZSDV-00064, Samograd, Korčula	1983.961
ZSDV-00066, Burinka, Crnopac	2205.754
ZSDV-00077, Velebita, Sjev. Velebit	1827.932
ZSDV-00081, Velebita, Sjev. Velebit	4939.723
ZSDV-00082, Ledena jama u Lomskoj Dulibi, Sjev. Velebit	3745.797

measured As concentration. Mobilized by the weathering of rocks and minerals As is thus readily fixed and accumulated in clays and in Fe and Al oxides in soils (Ure & Berrow, 1982). So its stronger correlation with precipitation, e.g. higher elevations is probably influenced by more intense transport of authigenic or allogenic clays, hydroxides and organic matter from the upper parts of the caves close or connected to the surface. A similar behavior can be concluded for K as a component of aluminosilicate minerals, including the clay minerals. Ca has negative correlation with elevation and precipitation (Table 12). It is weak but expected since caves located in higher and colder areas are less abundant in speleothems or there are no speleothem formations at all. Also, the differences between *r* considering elevation and precipitations can be used for rating of influences of temperature and precipitation on weathering, elements mobility and their incorporation in speleothems.

Factor 3 has excellent and very good correlations with Ni and Cr. Obviously, it is of a completely other origin than Factor 1, but most probably its origin is also natural (geogene), originating from flysch, which is known to be a source of Ni and Cr (Prohić et al., 1997; Miko et al., 2001; Frančišković-Bilinski et al., 2014). More about origin of Ni and Cr in studied speleothem samples will be presented in Discussion.

Table 9
Mean values of 10 elements and two other parameters for 3 obtained clusters. Element's contents are given in mg/kg, elevation in m and precipitation in mm/m^2.

	Cluster - no. 1 Mean	Cluster - no. 2 Mean	Cluster - no. 3 Mean
Pb	1.6	16.4	1.7
Zn	5.2	24.4	3.9
Ni	13.0	24.1	4.0
Cr	5.3	25.2	2.1
Co	0.8	4.7	0.6
Ca	347,837.5	255,923.0	368,921.8
Li	1.4	20.4	0.8
Al	949.4	14,651.5	429.0
Si	990.0	8148.5	472.2
Fe	903.7	12,177.5	399.4
Altitude z	572.0	1475.0	614.1
Precipitation	1465.0	1875.0	1461.3

Table 10
Factor loadings (varimax normalized; marked loadings are >0.70).

	Factor - 1	Factor - 2	Factor - 3
Pb	**0.838**	0.153	0.036
Zn	**0.759**	−0.173	0.301
Ni	0.067	−0.006	**0.987**
Cr	0.550	0.153	**0.781**
Co	**0.959**	0.143	0.154
Ca	**−0.867**	−0.112	−0.338
Li	**0.944**	0.262	0.138
Al	**0.944**	0.198	0.142
Si	**0.940**	0.236	0.115
Fe	**0.934**	0.188	0.147
z	0.253	0.888	0.078
Precipitation	0.093	**0.930**	3.45E−4
% of Expl.Var	6.867	**1.961**	1.893
Prp.Totl	0.572	0.163	0.158

4. Discussion

Our research shows that there are significant differences between concentrations of certain elements, which make them good candidates for further research. The correlation analyses included parameters such as elevation of cave entrance, overlays of speleothem location, geological composition of the area, climate zone and the actual amount of rainfall.

4.1. Mineral composition of speleothems

As already described in the Results, calcite is the only constituent of the majority of samples, with the note that traces of other minerals may be present, due to detection limits of XRD method. Only samples from the Cave system Lukina jama-Trojama (Velebit Mt.) show multi-mineral composition of several minerals, while samples at two other locations show presence of dolomite and at one location of quartz, besides calcite. Tremaine and Froelich (2013) and Wu et al. (2015) showed that the main chemical and mineral components of speleothems are quite similar to the host rock. This is because the main material source of drip water and speleothems are governed by the host rock. Their study revealed the main mineralogical and geochemical characteristics of host rock and speleothems, further discussing the seasonal variation of hydrochemical indices of drip water. So, in our study it could also be concluded that mineral composition of the studied speleothems reflects the composition of surrounding rocks. Around the location of Lukina

Table 11
Factor Scores for analyzed samples.

Sample	Cave	Region	Factor - 1	Factor - 2	Factor - 3
ZSDV-0001	Jopićeva špilja	Kordun	−0.30	−0.72	−0.44
ZSDV-0003	Lubuška jama	NP Sjeverni Velebit	−0.48	1.35	−0.22
ZSDV-0005	Špilja-rudnik Minjera	Supetar. Brač	−0.16	−0.80	−0.37
ZSDV-0006	Dolača	Žumberak	−0.25	−0.51	−0.45
ZSDV-0007	Golubnjača	Plitvice	−0.08	−0.32	−0.37
ZSDV-0009	Maklutača	Dugopolje	0.35	−0.42	−0.77
ZSDV-00010	Provala	Žumberak	−0.32	−0.72	−0.43
ZSDV-00011	Lukina jama	NP Sjeverni Velebit	3.76	0.47	0.74
ZSDV-00018	Markova špilja	Hvar	0.07	−1.42	−0.45
ZSDV-00039	Mandića špilja	Omiš	0.13	−1.55	1.47
ZSDV-00040	Manita Peć	NP Paklenica	−0.28	0.37	−0.42
ZSDV-00044	Munižaba	Crnopac	−0.58	1.29	−0.21
ZSDV-00045	Rača špilja	Lastovo	−0.12	−1.68	1.30
ZSDV-00046	Vodarica	NP Paklenica	−0.50	0.59	−0.22
ZSDV-00048	Jama Povajska Lipotica	Brač	−0.16	−0.97	−0.40
ZSDV-00053	Lukina jama	NP Sjeverni Velebit	1.10	1.12	−0.21
ZSDV-00054	Zagorska peć	Ogulin	−0.15	−0.06	−0.39
ZSDV-00055	Provala	Žumberak	−0.22	−0.75	−0.34
ZSDV-00056	Gvozdenica	Kordun	0.23	−0.98	−0.33
ZSDV-00058	Sedrena špilja iza mlina	Krka. Bilušić buk	−0.30	−0.67	−0.48
ZSDV-00059	Debeljača	Lovinac	−0.27	0.38	−0.46
ZSDV-00060	Nova Grgosova špilja	Otruševac	−0.25	−0.65	−0.43
ZSDV-00064	Samograd	Korčula	−0.18	−1.09	−0.41
ZSDV-00065	Špilja Barići	Kremen-Slunj	−0.27	−0.53	−0.37
ZSDV-00066	Burinka	Crnopac	−0.57	1.15	−0.39
ZSDV-00070	Fabrisova jama	Ročko polje. Istra	−1.23	−0.07	4.97
ZSDV-00072	Pčelina špilja	Gospić	−0.34	0.35	−0.23
ZSDV-00074	Kraljevska jama	Hvar	−0.10	−1.16	−0.18
ZSDV-00075	Vrelo	Fužine	−0.02	1.52	−0.28
ZSDV-00076	Meduza	NP Sjeverni Velebit	−0.89	1.49	1.42
ZSDV-00077	Velebita	NP Sjeverni Velebit	−0.47	1.46	0.13
ZSDV-00078	Velebita	NP Sjeverni Velebit	−0.31	1.38	−0.20
ZSDV-00081	Velebita	NP Sjeverni Velebit	−0.60	1.47	−0.48
ZSDV-00082	Ledena jama u Lomskoj dulibi	NP Sjeverni Velebit	−0.72	1.19	−0.22
ZSDV-00083	Lukina jama	NP Sjeverni Velebit	3.79	0.69	0.74
ZSDV-00084	Špilja u kamenolomu Tounj	Tounj	0.70	−0.42	−0.19
ZSDV-00085	Veternica	Medvednica	−0.01	−0.77	−0.40

Table 12
Correlation coefficients for elements, altitude and precipitation.

	Altitude z	Precipitation
Cd	−0.06	−0.06
Pb	0.34	0.22
Cu	0.28	0.10
Zn	0.12	−0.04
Mn	0.31	0.20
Ni	0.09	0.00
Cr	0.32	0.18
Co	0.37	0.22
Ba	0.40	0.21
Ca	−0.30	−0.20
K	0.42	0.39
Mg	0.02	−0.06
Na	0.14	0.45
Sr	−0.15	−0.14
Li	0.50	0.30
Mo	−0.03	−0.07
Sb	0.25	0.30
Bi	0.23	0.28
Be	0.41	0.25
Al	0.41	0.27
Tl	−0.18	−0.14
U	0.29	0.11
B	0.03	0.02
Si	0.45	0.30
Ti	0.45	0.26
W	0.42	0.18
Fe	0.42	0.26
V	0.13	0.28
Sn	0.16	0.02
As	0.59	0.42

jama cave the lithological composition is heterogeneous and at location of three samples with complex mineral composition among other lithological units carbonate breccias are present (Tari Kovačić and Mrinjek, 1994; Vlahović et al., 2007; Velić and Velić, 2009). So, it could be assumed that the identified minerals, such as quartz, chlorite, muscovite/illlite and plagioclase, originate from mica-chlorite matrix or quartz-carbonate cement, as part of present breccia.

4.2. Elemental composition of speleothems

Generally speaking, concentrations of all elements, especially of heavy metals in studied speleothems are very low. Even those two sampling media (speleothems and sediments) are different, when compared with available sediment quality criteria (SMSP and FALCONBRIDGE NC SAS, 2005) all the values of toxic elements are far below the toxic threshold values. Even anomalous values of speleothems from Lukina jama are below those values.

To get a better insight into the element distribution in the studied speleothems, several statistical analyses have been performed. Boxplot method was obtained to get anomalies. As already described in the Results section, most anomalies are present in samples from Lukina jama, especially in two speleothems samples: ZSDV-00011 and ZSDV-00083. Q-mode cluster analysis showed that those two samples are so much different regarding elemental compositions from any other samples, that they form a separate cluster (cluster 2). The third sample from Lukina jama belongs to cluster 1, although it has a rather high distance from cluster center (3051.135). Velebit Mt. is a coastal mountain chain, known to have Dfsbx climate according to Köppen-Geiger classification and high precipitation (1750–2000 mm/year) owing to prevalent western air currents and elevation. Those conditions are similar to those on Risnjak Mt. located 80 km NW from the Lukina jama area. Although in the soils of the Risnjak karst area increased concentrations of heavy metals caused by air-borne transport and precipitation from industrial areas of northern Italy were recorded (Vrbek and Gašparac, 1992; Vrbek et al., 1991, 1994), the study of clastic cave sediments from six caves did not show significantly increased concentrations of Pb and other heavy metals (Vrbek and Buzjak, 2004). Therefore recorded heavy metals content from cave sediments was attributed to natural origin. In a similar way increased concentrations of series of elements in Lukina jama are more likely to be of natural origin, due to specific composition of surrounding rocks. It can be supported by the comparison of heavy metal content in Lukina jama clastic cave sediments and speleothems (Table 13; Vrbek, 1995, 1998, 2007). The values are similar and can be used to support the thesis about their geogene origin. According to the heavy metal content in clastic cave sediments (sandy clay and clay) sampled at the depths between 928 and 1392 m below the surface, Lukina jama has very small quantities compared to some other caves in Croatia (Vrbek, 1995). Vrbek has recorded similar relations in caves with heavy metals concentrations similar to natural conditions and high concentrations as a result of anthropogenic pollution from dump sites and sewerage systems (Vrbek, 1986–1987; Vrbek, 1992-1993).

The Pb content in rocks is usually <20 mg/kg (Gerhardsson, 2004; Salminen et al., 2005) and in carbonate rocks worldwide and in Croatian

Table 13
Comparison of heavy metals content (mg/kg) in clastic sediments and speleothems of Lukina jama.

Type	Cd	Pb	Cu	Zn	Mn
Clastic sediments[a]	0.1–0.9	9–16	10–22	22–31	40–115
Speleothems	0.1–0.6	6.1–18.7	3.9–10	10.2–26.5	55.9–313

[a] After Vrbek (1998).

karst it is <10 mg/kg (Adriano, 1986; Bakšić et al., 2011; Hough, 2010; Kabata-Pendias, 2011; Lovrenčić Mikelić et al., 2013). Both Pb content in clastic cave sediments and speleothems in Lukina jama correspond to that value and therefore can be attributed to host rock origin. The analysis of the soil profiles shows that the main contamination is found in the upper 20–30 cm and decreasing with depth because the contaminants can migrate up to a few meters in depth in the soil profile but it is different for various metals and conditions. The migration depends on soil chemistry and texture (like pH, capacity of exchangeable cations, carbon and organic matter content, sand content, sorption/desorption processes of metals and metalloids on/from soil components), climate, topographical factors (like slope inclination) and biological activity (Sterckeman et al., 2000; Violante et al., 2010; Bakšić et al., 2011). In general it is considered that Pb in soil has limited mobility since after precipitation in the soil it quickly binds to the surface of the negatively charged particles which negatively affects Pb mobility and slowly converts to more insoluble forms such as sulfate, sulfide, oxide and phosphate salts. Therefore Pb concentration in cave sediments is lower than in surface soils (Bakšić et al., 2011). The mobility can rise when soluble organic complexes are formed or when the soil Pb exchange capacity approaches saturation. Extremely to significantly high Pb concentrations in karst springs in Croatian karst were recorded by Matić et al. (2012), as well as influence of Mn to Pb concentration (Matić et al., 2013). It is known that Pb has strong adsorption affinity for particles, especially for Mn oxides or carbonate (Bilinski et al., 1991; Gerhardsson, 2004; Feng, 2011). The significantly higher Mn amount in samples determined the higher Pb concentrations by adsorption of the most Pb onto Mn oxide particles. A similar connection was found in our samples, with strong correlation ($r = 0.82$) which also suggests geogene origin of Pb. The surface around the entrance of Lukina jama and its potential drainage basin that could feed speleothems has small quantities of topsoil or not at all (bare karst) so there is a small chance for absorption of aerosol Pb into organic soil components. One must also not neglect the depth of sampling locations to the length of the non-determinable flow paths, their interconnection influencing mixing from different sources and host rocks, different conditions influencing pH, temperature and deposition/denudation, and unknown water retention in voids during flow.

The only bigger difference is noticeable in Mn concentration with lower values in clastic sediments compared to speleothems. This is probably due to the very differing behavior of Mn in sediments controlled by various environmental factors. In a colder environment, like Lukina jama with average air temperature 3–4 °C (at the depth 1225 m below the surface; Paar et al., 2013a) Mn could be removed from the sediment by bicarbonates or as a complex with organic acids derived from decaying plants that could be influshed by water flows into the underground. Also the physical properties of Mn oxides and hydroxides result in their fast association with transitional metals like Cu, Zn, Pb. Also Mn^{2+} (aq) is readily soluble so its lower concentration in loose clastic sediment could also be a consequence of occasional flooding recorded in the lower epiphreatic parts of Lukina jama where sediments were sampled (Paar et al., 2013b).

According to Q-mode cluster analysis, all other studied samples (except those two from cluster 2) are rather equally distributed into clusters 1 and 3. Those two clusters show rather similar concentrations of most elements, with slightly higher values for most of them in cluster 1. But, when comparing those clusters with anomalous cluster 2, one can notice that concentrations of almost all elements are significantly higher in this cluster, for some elements up to 20 times. However, there are some exceptions, like Ca, Mo and B. Contrary to other elements, Ca has the lowest concentration in cluster 2, and even the differences to other clusters are not so high. Mo shows a completely different behavior than other elements, as it has 4 times higher concentration in cluster 1, while in anomalous cluster 2 it shows low concentrations, similar to those in cluster 3. B shows rather uniform concentrations in all three clusters. It is interesting to notice that all samples which show significant anomalies determined by boxplot method (besides those two which form separate cluster 2) belong to cluster 1 (one of samples from Lukina jama, Mandića cave, Špilja u kamenolomu Tounj cave, Fabrisova cave, Vrelo cave and Meduza cave). Caves with speleothems containing significant anomalies do not show any common characteristics: they do not belong to the same geomorphological category, do not belong to the same climate type and have different amounts of rainfall.

Sr is important as an indicator for fluid-rock interactions. Its variations in concentration are a result of precipitation rate, mineral stoichiometry, crystal growth mechanism, fluid composition and temperature. Calcite and dolomite in limestones have Sr concentrations 20–70 ppm (Banner, 1995).

Mg (Mn and Zn) incorporation in calcite is temperature dependent (Roberts et al., 1998; Fairchild and Treble, 2009) and also determined by drip water rate and chemistry (Huang and Fairchild, 2008) primarily determined by the host rock and soil cover. Besides that it is known that changes in the Mg concentration of a speleothem can be used to research air surface temperature changes especially in shallow caves where the calcite precipitation temperature and cave air temperature correspond to the annual mean of the surface air temperature (Gascoyne, 1983, 1992). So it can be presumed that speleothems from higher elevations will show different Mg concentration compared to caves located in lower elevations.

Si, Al, K, Na and Li can be used to determine if their high frequency oscillations might result from variations in the detrital (non-carbonate) content of the calcite e.g. clay particles and sands (Dandurand et al., 2011; Lovrenčić Mikelić et al., 2013; Tremaine and Froelich, 2013). In this case typical indices are concentrations of Al and K. This was supported by their strong positive correlation ($r = 0.85$). Similar strong relationships were recorded in the cases of Al with Si ($r = 0.94$) and Li ($r = 0.95$), and K with Si ($r = 0.87$) and Li ($r = 0.83$; Table 5).

4.3. Determination of flysch and terra rossa influence on speleothems

Our finding, obtained by factor statistical analysis that Ni and Cr are of other origin than other heavy metals is similar as the finding of Zupančič and Skobe (2014). They also concluded that the very high Cr and Ni levels found in their research could still be geogenic because soils developed on Eocene flysch rocks of the Istra region are enriched in both metals. Additional support to this is the finding of Lenaz et al. (2003), who state that detrital Cr-spinels are widespread in Eocene sandstones of the Brkini, Istra peninsula and Krk Island foredeep flysch basins. According to them, Cr-spinels were derived from the erosion of the Internal Dinarides, where type II and III peridotites are present, and also from the Outer Dinarides, where type I peridotites crop out. Frančišković-Bilinski et al. (2014) found elevated values of Cr and Ni in the flysch basins of Croatia and Slovenia. Miko et al. (2001) performed geochemical baseline mapping of soils developed on diverse bedrock from two regions in Croatia. In this research they concluded that the highest concentrations of both Cr and Ni in karst areas of Croatia are confined to three soil types: the terra rossa soils, the soils developed on Eocene flysch and the soils developed on Quaternary sands (on some islands). Both the Eocene flysch sedimentary rocks and Quaternary sands are probably partly derived from weathering products of basic magmatic rocks. A very high factor score is present in Fabrisova cave in Istra and somewhat lower, but also elevated scores are present also in Mandića cave. On those locations flysch is present in composition of the surrounding area in higher or lower amounts, so analysis supports this hypothesis. The hinterland of Fabrisova cave is built of Eocene flysch sediments, so it could be assumed that there are sources of Ni and Cr. Elevated scores in the case of Rača špilja (Lastovo Island) can't be explained in a similar way due to the absence of flysch, but it can be connected with terra rossa soils. For any deeper analyses further research is necessary.

5. Conclusions and recommendations

The Croatian karst, mostly part of Dinaric karst and worldwide known as the *locus typicus* of classical karst, is very rich in caves, which are very poorly investigated in terms of elemental and mineralogical composition of their speleothems. Therefore our research aims to determine "reference values" for the Croatian karst. The most important findings of our research are the following:

- Mineralogical analysis by XRD method showed that in 83.8% of studied speleothem samples calcite is the only identified mineral. In only 16.2% of samples some other minerals besides calcite (quartz, dolomite, chlorite, muscovite/illite, plagioclase) have been detected. Half of them (3 samples) are from Lukina jama, taken at different positions (with respect to depth), which is the cave with most complex mineralogical composition of speleothems. Two main sources of clays in caves are known: allogenic and authigenic. In case of samples from Lukina jama, the main source could be reworked fluvial deposit.
- Concentrations of 30 chemical elements are determined by ICP-MS method and their basic statistical parameters are calculated to get a brief insight into the concentration ranges of studied elements in the studied caves that belong to the Croatian karst. These values could serve as a database and as "reference values" for the Croatian karst that can be compared with values determined in some other karst regions worldwide.
- Elemental concentrations obtained for each speleothem sample in this work are average values for the whole time of speleothem growth, as each speleothem can encompass long period of precipitation, with several climate and environmental settings. Average samples from each speleothem were obtained in a way that whole speleothems specimens were crushed and homogenized in a mortar.
- We also aimed to determine differences of concentrations of particular elements in speleothems of different locations and to define parameters which might be possible causes of those differences, keeping in mind the fact that all speleothems are not equally old and didn't have the same growth dynamic. Our conclusion, which has to be additionally proved by future investigations, is that differences in environmental conditions (geologic, geomorphologic, soil, hydrologic, climatic, vegetational) condition variations of element concentration in the speleothems.
- The largest number of element anomalies, obtained by boxplot method, is present in all three samples from Lukina jama located on Northern Velebit Mt. In this cave a whole series of elements, including many heavy metals, show extreme values (Pb, Cu, Zn, Mn, Ni, Cr, Co, Ba, K, Mg, Li, Be, Al, U, Si, Ti, W, Fe, As). This is the deepest of the investigated caves, with heterogeneous lithological and mineralogical composition, which has obviously influenced increased concentrations of series of elements. Further investigations of influence of rock and mineral composition and environmental conditions on elemental concentrations of speleothems would be important.
- All statistical analyses performed in this research showed as very useful, as following: Basic statistical parameters are very useful as "reference values" of the whole studied Croatian karst region; Boxplot was a very suitable method to determine caves with anomalous concentrations of particular elements; Cluster analysis of Q-mode was ideal to find groups of samples of similar properties; Factor analysis was a method of choice to reduce the number of variables and to set up a model of several factors, each of them describing one anthropogenic or natural influence (e.g. Cr—Ni related factor indicating influence of flysch or terra rossa soils) and to estimate the strength of each factor in each sample; Pearson's correlation matrix was most suitable to study the strength of linear correlation of mass fractions between researched elements and to determine influences of similar sources. Therefore, we recommend such multi-statistical method approach for similar research in the future.
- The Croatian karst is not so large area in global proportions, but its particular parts are rather different due to local geology, geomorphological processes, climate conditions, precipitation and other environmental factors. Therefore, in one of directions of our future research, which is in progress, we will orient to deep caves, where our research focus will be aimed to investigate relations of rock composition, sediments and speleothems and try to determine relation of elemental composition of speleothems with different periods of speleothem formation. Elements which will be determined to be influenced by climatic and hydrological conditions will be proposed as suitable for paleoclimatic research.
- This study was the first study of such type performed in such a broad area of the Croatian karst. Therefore we hope that the obtained results will contribute the knowledge about elemental and mineralogical composition, which are mostly determined by geogene influence. Knowledge of natural ("zero") state of nature is very important because of nature protection measures and it will enable future monitoring and easier detection of possible anthropogenic influence in the future. There are still many unsolved questions, therefore the current paper should be considered as initiation of future broader research, which should include the different temporal resolution of speleothem proxy time series.

Acknowledgements

This research was partially supported by the Northern Velebit National Park (2010-2016) and the Environmental Protection and Energy Efficiency Fund, Croatia (2010-2016) and research funding in the Department of Geography at the Faculty of Science, University of Zagreb (2015). We thank the members of the Speleological Society Velebit and Speleological Committee of CMA, Zagreb, for their assistance in field work. We thank Prof. Nenad Tomašić for assistance with mineralogical analysis, and Andrej Stroj, PhD, for geological profile of Lukina jama. We thank Tatjana Jauk, B·Sc., a professional linguist, for her kind help in editing the English language of this manuscript.

References

Adriano, D.C., 1986. Trace Elements in Terrestrial Environments. Springer-Verlag, Berlin.
Allan, M., Fagel, N., Van Rampelbergh, M., Baldini, J., Riotte, J., Chenge, H., Edwards, R.L., Gillikin, D., Quinif, Y., Verheyden, S., 2015. Lead concentrations and isotope ratios in speleothems as proxies for atmospheric metal pollution since the industrial revolution. Chem. Geol. 401, 140–150.
Babić, L., Lacković, D., Horvatinčić, N., 1996. Meteoric phreatic speleothems and the development of cave stratigraphy: an example from Tounj cave, Dinarides, Croatia. Quat. Sci. Rev. 15, 1013–1022.
Bahun, S., 1970. Geological basis of the Ogulin-Plaški karst depression. KRŠ Jugosl. 7/1, 1–20.
Bakšić, D., Perković, I., Pernar, N., Vukelić, J., Vrbek, B., 2011. Pedophysiographic features and heavy metal content (Pb, Zn, Cd and Cu) in spruce forests of Northern Velebit and Štirovača. Croat. J. For. Eng. 32/1, 111–120.
Banner, J.L., 1995. Application of trace element and isotope geochemistry of strontium to studies of carbonate diagenesis. Sedimentology 42, 805–824.
Bilinski, H., Kozar, S., Plavšić, M., Kwokal, Ž., Branica, M., 1991. Trace metal adsorption on inorganic solid phases under estuarine conditions. Mar. Chem. 32, 225–234.
Bočić, N., 2006. Deepest Caves of Croatian Karst and Their Basic Geomorphological Features [in Croatian]. Međunarodni znan. skup "Akademik Josip Roglić i njegovo djelo", Zbornik radova. Hrv. geogr. društvo, Zagreb, Hrvatska, pp. 161–182.
Bognar, A., Faivre, S., Buzjak, N., Pahernik, M., Bočić, N., 2012. Recent Landform Evolution in the Dinaric and Pannonian Regions of Croatia. In: Lóczy, D., et al. (Eds.), Recent Landform Evolution: The Carpatho–Balkan–Dinaric Region. Springer Geography, pp. 313–344.
Boldrin, A., Juračić, M., Mengazzo Vitturi, L., Rabitti, S., Rampazzo, G., 1992. Sedimentation of river-borne material in a shallow shelf sea: Adiga River, Adriatic Sea. Mar. Geol. 103, 473–485.
Bonacci, O., 1987. Karst Hydrology: With Special Reference to Dinaric Karst. Springer-Verlag, Berlin.
Borsato, A., Frisia, S., Fairchild, I., Somogyi, A., Susini, J., 2007. Trace element distribution in annual stalagmite laminae mapped by micrometer-resolution X-ray fluorescence:

implications for incorporation of environmentally significant species. Geochim. Cosmochim. Acta 71, 1494–1512.
Dandurand, G., Maire, R., Ortega, R., Devès, G., Lans, B., Morel, L., Perroux, A.-S., Vanara, N., Bruxelles, L., Jaillet, S., Billy, I., Martinez, P., Ghaleb, B., Valla, F., 2011. X-ray Fluorescence Microchemical Analysis and Autoradiography Applied to Cave Deposits: Speleothems, Detrital Rhythmites, Ice and Prehistoric Paintings. Géomorphologie: Relief, Processus, Environnement Vol. 4/2011 pp. 407–426.
Davis, J.C., 2002. Statistics and Data Analysis in Geology. third ed. John Wiley & Sons.
Domínguez-Villar, D., Fairchild, I., Baker, A., Carrasco, R., Pedraza, J., 2013. Reconstruction of cave air temperature based on surface atmosphere temperature and vegetation changes: implications for speleothem palaeoclimate records. Earth Planet. Sci. Lett. 369–370, 158–168.
Fairchild, I.J., Baker, A., 2012. Speleothem Science. From Process to Past Environments. Wiley-Blackwell.
Fairchild, I.J., Treble, P.C., 2009. Trace elements in speleothems as recorders of environmental change. Quat. Sci. Rev. 28, 449–468.
Fairchild, I.J., Borsato, A., Tooth, A.F., Frisia, S., Hawkesworth, C.J., Huang, Y., McDermott, F., Spiro, B., 2000. Controls on trace element (Sr–Mg) compositions of carbonate cave waters: implications for speleothem climatic records. Chem. Geol. 166, 255–269.
Fairchild, I.J., Smith, C.L., Baker, A., Fuller, L., Spötl, C., Mattey, D., McDermott, F., 2006. Modification and preservation of environmental signals in speleothems. Earth Sci. Rev. 75, 105–153.
Feng, J.L., 2011. Trace elements in ferromanganese concretions, gibbsite spots, and the surrounding terra rossa overlying dolomite: their mobilization, redistribution and fractionation. J. Geochem. Explor. 108, 99–111.
Filipčić, A., 1998. Climatic regionalization of Croatia according to W. Köppen for the standard period 1961–1990 in relation to the period 1931–1960 [in Croatian]. Acta Geogr. Croat. 33, 1–15.
Ford, D.C., Williams, P.W., 2007. Karst Geomorphology and Hydrology. second ed. John Wiley & Sons, Chichester, U.K.
Frančišković-Bilinski, S., Scholger, R., Bilinski, H., Tibljaš, D., 2014. Magnetic, geochemical and mineralogical properties of sediments from karst and flysch rivers of Croatia and Slovenia. Environ. Earth Sci. 72, 3939–3953.
Garašić, M., 1992. Hematite from clastic sediments of the cave Vrelo, its genesis and tectonic-structural relationship to closer caves (Gorski kotar) [in Croatian]. Spelaeologia Croat. 3, 27–31.
Gascoyne, M., 1983. Trace element partition coefficients in the calcite-water system and their paleoclimatic significance in cave studies. J. Hydrol. 61, 213–222.
Gascoyne, M., 1992. Palaeoclimate determination from cave calcite deposits. Quat. Sci. Rev. 11, 609–632.
Gázquez, F., Claforra, J.M., Forti, P., 2011. Black Mn-Fe crusts as markers of abrupt palaeoenvironmental changes in El Soplao Cave (Cantabria, Spain). Int. J. Speleol. 40 (2), 163–169.
Gerhardsson, L., 2004. Lead. In: Merian, E., Anke, M., Ihnat, M., Stoeppler, M. (Eds.), Elements and Their Compounds in the EnvironmentMetals and Their Compounds vol. 2. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, pp. 879–900.
Halamić, J., Peh, Z., Bukovec, D., Miko, S., Galović, L., 2001. A factor model of the relationship between stream sediment geochemistry and adjacent drainage basin lithology, Medvednica Mt. Croat. Geol. Croat. 54, 37–51.
Hill, C.A., Forti, P., 1997. Cave Minerals of the World. second ed. National Speleological Society, Huntsville, Ala.
Hough, R.L., 2010. Copper and Lead. In: Hooda, P.S. (Ed.), Trace Elements in Soils. Wiley, pp. 441–460.
Huang, Y., Fairchild, I.J., 2008. Annual trace element records in speleothems from Grotta di Ernesto, NE Italy. Mineral. Mag. 62A, 661–662.
Ihlenfeld, C., Norman, M.D., Gagan, M.K., Drysdale, R.N., 2003. Climatic significance of seasonal trace element and stable isotope variations in a modern freshwater tufa. Geochim. Cosmochim. Acta 67, 2341–2357.
Kabata-Pendias, A., 2011. Trace Elements in Soils and Plants. CRC Press, Boca Raton.
Kaufman, L., Rousseeuw, P., 1990. Finding Groups in Data. John Wiley & Sons, New York.
Korbar, T., 2009. Orogenic evolution of the external Dinarides in the NE Adriatic region: a model constrained by tectonostratigraphy of Upper Cretaceous to Paleogene carbonates. Earth Sci. Rev. 96 (4), 296–312.
Kuhta, M., Bakšić, D., 2001. Karstification Dynamics and Development of the Deep Caves on the North Velebit Mt. – Croatia. 13th International Congress of Speleology, Proceedings, Sociedade Barsiliera de Espeleologia, Brasilia, pp. 1–4.
Lacković, D., Glumac, B., Asmerom, Y., Stroj, A., 2011. Evolution of the Veternica Cave (Medvednica Mountain, Croatia) drainage system: insights from the distribution and dating of cave deposits. Geol. Croat. 64 (3), 213–221.
Lenaz, D., Kamenetsky, V.S., Princivalle, F., 2003. Cr-spinel supply in the Brkini, Istrian and Krk Island flysch basins (Slovenia, Italy and Croatia). Geol. Mag. 140 (3), 335–342. http://dx.doi.org/10.1017/S0016756803007581.
Lorens, R.B., 1981. Sr, Cd, Mn and Co distribution coefficients in calcite as a function of calcite precipitation rate. Geochim. Cosmochim. Acta 45, 553–561.
Lovrenčić Mikelić, L., Oreščanin, V., Barišić, D., 2013. Distribution and origin of major, minor, and trace elements in sediments and sedimentary rocks of the Kaštela Bay (Croatia) coastal area. J. Geochem. Explor. 128, 1–13.
Matić, N., Cuculić, V., Frančišković-Bilinski, S., 2012. Investigations of karstic springs of the Biokovo Mt. from the Dinaric karst of Croatia. Chem. Erde 72, 179–190.
Matić, N., Cuclić, V., Frančišković-Bilinski, S., 2013. Geochemical and isotopic characteristics of karstic springs in coastal mountains (Southern Croatia). J. Geochem. Explor. 132, 90–110.
Miko, S., Halamić, J., Peh, Z., Galović, L., 2001. Geochemical baseline mapping of soils developed on diverse bedrock from two regions in Croatia. Geol. Croat. 54 (1), 53–118.
Morrison, D.F., 1967. Multivariate Statistical Methods. Mc Graw-Hill, New York.
Onac, B., 1996. Mineralogy of speleothems from caves in the Padurea Craiului Montains (Romania) and their paleoclimatic significance. Cave Karst Sci. 23 (3), 109–124.
Onishi, H., Sandell, E.B., 1955. Geochemistry of arsenic. Geochim. Cosmochim. Acta 7, 1–33.
Oster, J., Montanēz, I., Kelley, P., 2012. Response of a modern cave system to large seasonal precipitation variability. Geochim. Cosmochim. Acta 91, 92–108.
Paar, D., Stroj, A., Mudronja, L., 2012. Speleološka ekspedicija "Lukina jama 2011", Hrvatski speleološki poslužitelj – zbornik radova, Vol. 2, Br. Vol. 2 pp. 70–74.
Paar, D., Buzjak, N., Bakšić, D., Radolić, V., 2013a. Physical Research in Croatia's Deepest Cave System Lukina jama-Trojama, Mt·Velebit. 16th Int. Congress of Speleology, Proceedings vol. 2. Czech Speleological Society and UIS, Brno, pp. 442–446.
Paar, D., Stroj, A., Buzjak, N., Bakšić, D., Lacković, D., Ujević Bošnjak, M., Radolić, V., Kljajo, D., 2013b. Scientific Research in the Cave System Lukina jama – Trojama (-1421) on the Velebit Karst Massif (Croatia). 21th International Karstological School, Guidebook & Abstracts, Postojna, IZRK SAZU, p. 77.
Peel, M.C., Finlyanson, B.L., McMahon, T.A., 2007. Updated world map of the Köppen-Geiger climate classification. Hydrol. Earth Syst. Sci. 11, 1633–1644.
Powder Diffraction File, 1997. International Center for Diffraction Data, Newtown Square, PA.
Prohić, E., Hausberger, G., Davis, J.C., 1997. Geochemical patterns in soils of the karst region, Croatia. J. Geochem. Explor. 60, 139–155.
Rau, G., Cuthbertb, M., Andersen, M., Baker, A., Rutlidge, H., Markowska, M., Roshan, H., Marjo, C., Graham, P., Acworth, I., 2015. Controls on cave drip water temperature and implications for speleothem-based paleoclimate reconstructions. Quat. Sci. Rev. 127, 19–36.
Reimann, C., Filzmoser, P., Garrett, R.G., 2005. Background and threshold: critical comparison of methods of determination. Sci. Total Environ. 346, 1–16. http://dx.doi.org/10.1016/j.scitotenv.2004.11.023.
Roberts, M., Smart, P.L., Baker, A., 1998. Annual trace element variations in a Holocene speleothem. Earth Planet. Sci. Lett. 154 (1–4), 237–246.
Rudzka, D., Mcdermott, F., Surić, M., 2012. A late Holocene climate record in stalagmites from Modrič Cave (Croatia). J. Quat. Sci. 27 (6), 585–596.
Salminen, R. (Chief-editor), Batista, M. J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Lima, A., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P. J., Olsson, S.Å., Ottesen, R.-T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A., Tarvainen, T. 2005. Geochemical Atlas of Europe. Part 1: Background Information, Methodology and Maps. Espoo, Geological Survey of Finland, http://www.gtk.fi/publ/foregsatlas/ (01. 10. 2015.)
SMSP and FALCONBRIDGE NC SAS, 2005. Koniambo Project, Environmental and Social Impact Assessment, Chapter 4 Mine, 4.2–7 Quality Criteria for Freshwater Sediment.
StatSoft, Inc, 2001. STATISTICA (data analysis software system). (version 6) www.statsoft.com.
Sterckeman, T., Douayb, F., Proixa, N., Fourrierb, H., 2000. Vertical distribution of Cd, Pb and Zn in soils near smelters in the North of France. Environ. Pollut. 107, 377–389.
Stroj, A., Velić, I., 2015. Geological profile of Cave system Lukina Jama-Trojama on Northern Velebit. 5th Croatian Geological Congress With International Participation, Abstracts Book, Croatian Geological Survey, pp. 240–241.
Surić, M., Horvatinčić, N., Suckow, A., Juračić, M., Barešić, J., 2005a. Isotope records in submarine speleothems from the Adriatic coast, Croatia. Bull. Soc. Géol. Fr. 176 (4), 363–373.
Surić, M., Juračić, M., Horvatinčić, N., Krajcar Bronić, I., 2005b. Late Pleistocene-Holocene sea-level rise and the pattern of coastal karst inundation - records from submerged speleothems along the Eastern Adriatic Coast (Croatia). Mar. Geol. 214 (1/3), 163–175.
Surić, M., Richards, D.A., Hoffmann, D.L., Tibljaš, D., Juračić, M., 2009. Sea level change during MIS 5a based on submerged speleothems from the eastern Adriatic Sea (Croatia). Mar. Geol. 262, 62–67.
Surić, M., Roller-Lutz, Z., Mandić, M., Krajcar Bronić, I., Juračić, M., 2010. Modern C, O, and H isotope composition of speleothem and dripwater from Modrič Cave, eastern Adriatic coast (Croatia). Int. J. Speleol. 39 (2), 91–97 (2010).
Surić, M., Lončarić, R., Buzjak, N., Shultz, S.T., Šangulin, J., Maldini, K., Tomas, D., 2015. Influence of submarine groundwater discharge on seawater properties in Rovanjska-Modrič karst region (Croatia). Environ. Earth Sci. 74 (7), 5625–5638.
Tari Kovačić, V., Mrinjek, E., 1994. The role of Palaeogene clastics in the tectonic interpretation of Northern Dalmatia (Southern Croatia). Geol. Croat. 47 (1), 127–138.
Tremaine, D.M., Froelich, P.N., 2013. Speleothem trace element signatures: a hydrologic geochemical study of modern cave dripwaters and farmed calcite. Geochim. Cosmochim. Acta 121, 522–545.
Tukey, J.W., 1977. Exploratory Data Analysis. Addison-Wesley, Reading, PA.
Ure, A.M., Berrow, M.L., 1982. The elemental constituents of soils. In: Bowen, H.J.M. (Ed.), Specialist Periodical Report Environmental Chemistry Vol.2. Royal Society of Chemistry, London (Snr. Reporter).
Velić, I., Velić, J., 2009. From Marine Shallows to the Mountain: Geological Guidebook Through the Northern Velebit National Park. NP Sjeverni Velebit, Krasno.
Verheyden, S., 2004. Trace elements in speleothems: a short review of the state of the art. Int. J. Speleol. 33 (1/4), 95–101.
Violante, A., Cozzolino, V., Perelomov, L., Caporale, A.G., Pigna, M., 2010. Mobility and bioavailability of heavy metals and metalloids in soil environments. J. Soil Sci. Plant Nutr. 10 (3), 268–292.
Vlahović, I., Tišljar, J., Velić, I., Matičec, D., 2005. Evolution of the Adriatic carbonate platform: palaeogeography, main events and depositional dynamics. Palaeogeogr. Palaeoclimatol. 220 (3–4), 333–360.
Vlahović, I., Velić, I., Tišljar, J., Matičec, D., 2007. Jelar breče, OUGSME GEO-TRIP 2007, Guidebook. pp. 21–23.

Vrbek, B., 1986–1987. Results of soil survey in the cave system Đula-Medvedica [in Croatian]. Speleology XXXIV-XXXV, 35–38.
Vrbek, B., 1995. The Content of Heavy Metals in Sediment of Cave System Lukina jama-Trojama [in Croatian]. Report, p. 4 (www.speleologija.eu (1. 9. 2015.)).
Vrbek, B., 1998. Contribution to the study of heavy metals in sediments of the cave system Lukina jama-Trojama on Velebit [in Croatian]. Works Croat. For. Res. Inst. 33 (1), 95–106.
Vrbek, B., 2007. The Chemical Characteristics of Cave Sediments [in Croatian]. In: Bakšić, D., Barišić, T., Božić, V., Buzjak, S., Čaplar, A., Jalžić, B., Lacković, D., Stroj, A., Šmida, B., Vrbek, B., M., V. (Eds.), Cave System Lukina jama-Trojama, Zagreb, HPS, pp. 75–76.
Vrbek, B., Buzjak, N., 2004. Contribution to the knowledge of the content of heavy metals (Pb, Cu, Zn) in speleological objects in the Risnjak National Park (Croatia). Acta Carsologica 33 (2), 183–188.
Vrbek, B., Gašparac, M., 1992. New findings of imissions of heavy metals in the National Park Risnjak [in Croatian]. Rad. Šumar. Inst. 27 (1), 65–75.
Vrbek, B., 1992. the chemical and physical characteristics of the sediments of some caves in Croatia [in Croatian]. Speleology 40 (41), 46–48.
Vrbek, B., Vrbek, M., Vukelić, J., 1991. The Acidification of Soil and the Accumulation of Pb, Cu i Zn in Fir Communities of Risnjak NP [in Croatian]. Šumarski List Vols. 115, 3–5 pp. 163–172.
Vrbek, B., Vrbek, M., Vukelić, J., Gašparac, M., 1994. Results of the Research of Heavy Metals Input (Pb, Cu, Zn) in the National Park Risnjak [in Croatian], 40. Years of National Park Risnjak Proceedings of Papers, pp. 140–142.
Wu, K., Shen, L., Zhang, T., Xiao, Q., Wang, A., 2015. Links between host rock, water, and speleothems of Xueyu Cave in Southwestern China: lithology, hydrochemistry, and carbonate geochemistry. Arab. J. Geosci. http://dx.doi.org/10.1007/s12517-015-1876-6.
Zaninović, K., Gajić-Čapka, M., Perčec Tadić, M., 2008. Klimatski Atlas Hrvatske/Climate Atlas of Croatia 1961–1990., 1971–2000. Državni hidrometeorološki zavod, Zagreb.
Zupan Hajna, N., 2011. Dinaric Karst: Geology and Geography. In: White, W., Culver, D. (Eds.), Encyclopedia of Caves. Elsevier, pp. 195–203.
Zupančič, N., Skobe, S., 2014. Anthropogenic environmental impact in the Mediterranean coastal area of Koper/Capodistria, Slovenia. J. Soils Sediments 14, 67–77. http://dx.doi.org/10.1007/s11368-013-0770-7.