Bat Guano Influence on the Geochemistry of Cave Sediments from Modrič Cave; Croatia

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Abstract

The entrance to the Modrič cave is located at the altitude of 30 m above sea level some 70m away from the major coastal highway Rijeka-Zadar in Croatia. The cave was formed within Cretaceous limestones, and is characterized by slightly inclined to horizontal chambers and channels, which have a total length of 829 m. Baseline contents of elements both in sediments and percolating waters were determined. Silty loams with guano contain abundant quartz, illite and taranakite and minor vivianite and high concentrations of Cu (2869 mg/kg), Zn (951 mg/kg) and Cd (28 mg/kg). Also sediments mixed with guano are enriched with light REE as well as elevated concentrations of U, Th, Rb and Hg in comparison with local topsoil. Sediments with bone fragments contain abundant quartz, illite, calcite and hydroxylapatite and minor carndallite and lower contents of heavy metals. All sediments analysed showed various degrees of contamination by Cu and Zn from dispersed guano.

Introduction

The entrance to Modrič cave locted in the central part of the Croatian coastal region was used by local population as a natural shelter for centuries, but the underground network of channels and chambers was discovered in 1985. Since the cave was naturally sealed from its entrance an opening was chiseled through opened fissures in the limestone. The local authorities managed to prevent devastation of speleothems by controlling of entries made to the cave system. The favorable morphology and numerous stalagmites, pillars, flowstone, helictites, draperies (KUHTA et al., 1999) etc., as well as the paleontologic and archeological remnants (MALEZ, 1987) preserved in the cave sediments made it attractive as tourist destination. Therefore a comprehensive study, which included mapping, analysis of waters, and cave sediments, as well as age determinations (KUHTA et al., 1999) was undertaken to evaluate the baseline conditions within the cave before its utilization.

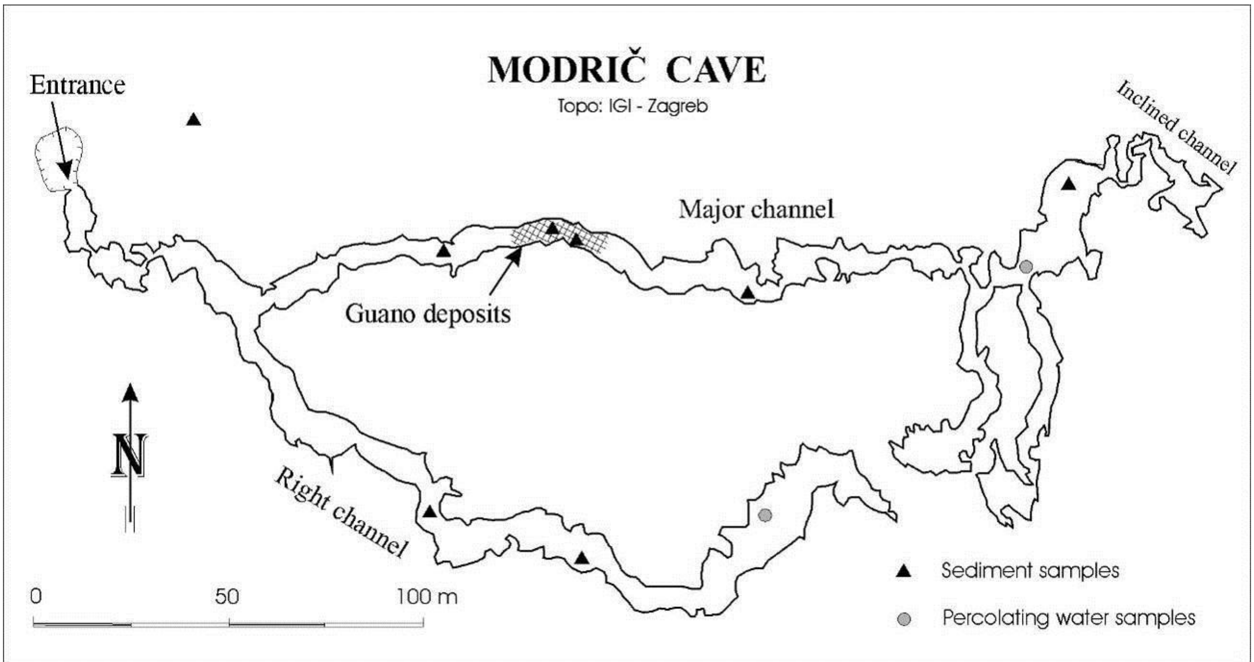

Fig. 1 Location of samples from the Modrič cave.

The vicinity of a major highway and recent war activities (1991/1992), implied to possible negative impacts on this vulnerable environment. The frequent occurrence of a thin dark crust on the floors in most depressions and on sediments was especially interesting in this sense. This was determined to be finely dispersed guano. Guano (bat guano, bird guano, penguin guano) similar to phosphates in general is a well-known source of heavy metals.

Heavy metal movement with water in sediments and soils requires that the metals be in soluble phase or associated with mobile particles and as such can have impacts on the quality of ground water. The objective of this study was the investigation of heavy metal concentrations and the movement of elements derived from bat guano in a cave environment.

Geology, Hydrogeology and Cave Morphology

Modrič cave formed within the Cenomanian-Turonian well bedded limestones. The limostenes consist of poorly sorted bioclasts with a dense sparite matrix. Within the beds the occurrence of the lamellibranchiata *Chondrondonta joannae* is quite frequent. The layers often contain lenses of platy limestones containing foramenifera and rarely macrofossils. The youngest quaternary beds that cover the bedrock are thin chromic cambisols, which accumulated in openings of karstified fissures and local depressions.

The wider region of the cave is located within the contact zone of the Adriatic carbonate platform structural complex and the Dinaric carbonate platform. The surface manifestation of the contact zone is a 2.5 km wide fault zone termed the Velebit fault (HERAK, 1986). This regional tectonic structure consists of a series of parallel faults with a general strike NW-SE, two of these faults are located to the north and to the south of the cave. The limestone beds have a general strike NW-SE with a dip angles ranging from 20 to 40°and inclination towards the NW. The faults and numerous networks of tectonic fissures formed during several tectonic events that shaped the morphology of the landscape had a key role in the formation of subsurface karst phenomena including Modrič cave.

The cave is located within a series of well permeable highly karstified carbonate rocks. The surrounding karst is characterised by the absence of surface flows and a fast direct infiltration of precipitation waters and a development of complex underground geomorphologic features. The infiltrated precipitation waters are drained through the complex systems of karstified fissures directly towards the sea. There are no concentrated discharges of fresh water along the coast so outflow of the water probably occurs in a depressive manner. The cave is located above groundwater level and outside the present zone of active circulation. The dimensions of the underground chambers indicate an important hydrogeological role of this region in the geological past. Modrič cave formed as a consequence of groundwater activity, during which groundwater flowed from the regional Velebit Mt. karst aquifer towards the terrain located at lower altitudes, i.e. towards the morphological depression of the present sea channel the Velebit channel. Active parts of this system exist near by in the form of submarine springs Modrič (-30 m) and Zečica (-45 m) and the coastal spring Velebit.

The entrance to the cave (1.8m x 1.3m) is located at the altitude of 30 m above sea level some 110m away from a major coastal highway Rijeka-Zadar. The basic morphological features of the cave are slightly inclined to horizontal chambers and channels, which have been explored in the total length of 829 m. From the entrance the cave extends generally towards the east. The elevation difference from the lowest point in the middle of the Major channel (Glavni kanal) and the highest point in the inclined channel (Kosi kanal) is 29 m. In most parts of the cave the width of the passages ranges from 2 to 8 m and in parts extends up to 14m. As a consequence of stalagmite formation and flowstone deposition on several places the channels were almost closed so it was necessary to widen them. The sediment deposits are found in larger chambers and varies depressions within the cave. The sediments are mainly silt loams and clay silt loams of reddish-brown to brown colour (5YR to 7.5YR), with calcareous debris and numerous bone fragments of Holocene fauna (*Ursus Spelaeus*), human bone remains and remnants of eneolithic pottery (MALEZ, 1987). The structure of the sediments is quite chaotic, lacking visible stratification, with variable thickness from several centimetres to probably over 1.5m. Dark brown and white bat guano deposits occur in several places covering the sediments up to 1 m over a surface of several square meters (central part of the main-Glavni kanal-channel). A thin grey layer that covers the damp sediments and the floor of the cave was determined to be of finely dispersed guano. The bats are not frequent residents of the cave today, since the entrance was first opened in 1985.

Methodology

Typical sediment samples (sediments with bone fragments from various depths from the sediment profile, sediments mixed with guano, dark mud coatings over sediments and dark crusts with dissolution surfaces on flowstone) and soil samples from the surface above the cave were selected for geochemical and mineralogical analyses. The objective of the geochemical study was to determine the baseline concentrations of elements (total and aqua regia extraction), their mobility and mineral phases (sequential extraction) that control their mobility and to asses possible anthropogenic influences especially as a consequence of heavy traffic from the nearby highway. Detailed analysis of 20 cave sediment samples was performed.

Major and trace element values including REE were obtained after $LiBO_3$ fusion by ICP-MS, also additional analysis were performed after *aqua regia* (HNO_3: HCl, 1:3) extraction to verify the high heavy metal contents in the sediments. The residence sites of metals in the sediments were identified by sequential extraction performed with the aid of a modified combination of procedures proposed by TESSIER et al., (1979) and HALL et al., (1996). Sequential extraction of the sediment samples was performed to give the following five fractions: adsorbed (AD), bound to carbonate (CC), bound to iron and manganese oxides (FEMN), bound to organic matter and sulphides (OR) and residual (RES). The amount of exchangeable fractions of elements was determined after extraction with 1M KCl. All solutions were analysed for Zn, Cu, Fe, Mn, P and Ni by a Jobin Yvon 50P simultaneous inductively coupled plasma-atomic emission spectrophotometer (ICP-AES) and Pb and Cd by a Pye Unicam SP9 flame atomic absorption spectrophotometer (AAS) using an air-acetylene flame. Filtered (-45μm) samples of percolating drop water were analysed by ICP-MS. Mineral composition of selected samples was analysed with a Philips diffractometer (CuKα radiation) equipped with a graphite monocromator and proportional counter.

Results and Discussion

The X-ray diffraction analysis showed that the acid (pH<3) sediments with variable contents of guano contain abundant quartz , illite and taranakite and minor vivianite, the almost "pure" guano sample had a similar composition but amorphous matter prevails. Sediments (bone fragments present) with no visible guano presence (pH>6) contain abundant quartz, illite, calcite and hydroxylapatite with scarce carndallite. The dark crusts with dissolution surfaces on flowstone consist of fibrous (2mm below the surface) and pinkish white earthy masses (5-10mm wide) of hydroxylapatite and sporadic calcite. From the chemical analysis results of total contents of elements ($LiBO_3$ fusion) in Table 1 it is visible that, P_2O_5, Cu, Zn, Th, U, Sb and Cd have higher concentration in cave sediments especially those under the direct influence of bat guano. *Aqua regia* extraction of 12 sediment samples from various depths and locations within the cave gave Cu concentrations ranging from 34 to 450 mg/kg, Zn from 181 to 1181 mg/kg and Cd from 0.3 to 4.3 mg/kg. Almost "pure" bat guano contained high concentrations of Cu (2869 mg/kg), Zn (951 mg/kg) and Cd (28 mg/kg). Very high concentrations of these elements (Zn 1181 mg/kg; Cu 385 mg/kg; Cd 4.3 mg/kg) were found in the dark fine mud coatings (approximately 5mm thick) that cover most of the floor sediments. These coatings are finely dispersed guano deposited by water in various pools and depressions. The content of these metals is usually much lower in sediments from deeper parts of the cave sediment profiles especially Cu whereas Zn concentrations are regularly elevated (in comparison to topsoil). Namely sediments from deeper horizons do not contain neither guano nor minerals derived from it but contain only quartz, illite, calcite minor feldspar and also some bone apatite. Although bat guano contains 2869 mg/kg of Cu only 0.7 mg/kg (0.03%) were extracted by 1M KCl while at the same time 78 mg/kg of Zn were extracted from a total of 951 mg/kg (i.e. 8.2 % of exchangeable Zn) also due to the acidy of these sediments the mobility of Al was also high. Therefore it is possible that the waters that percolate through the guano into deeper parts of the profile carry much more Zn and accumulate it there. Copper is obviously less mobile and retained in the surface layers. The sediment samples also contain higher concentrations of U and Ba as well as Hg (sediments with guano 790 μg/kg, topsoil 405 μg/kg). The distribution of rare earth elements in cave sediments with guano shows a slight enrichment of light rare earths (LREE) in comparison to European shale (ES) and depletion of heavy rare earths (HREE), while sediments and topsoil in general have similar distribution pattern to ES with only a slight enrichment of La in topsoil (Fig. 2).

Some of the percolating waters collected from the ceiling were also found to be enriched in these elements. The "uncontaminated" filtered (-45μm) waters contained in average 2 μg/L of Zn, 0.012 μg/L of Cd, 0,4μg/L of Cu and 0.08 μg/L La, 0.04μg/L of Ce, while the guano polluted filtered drop water contained 22 μg/L of Zn, 0.46 μg/L of Cd, 3,5μg/L of Cu and 0.157 μg/L La, 0.29 μg/L of Ce, a several fold increase. These waters were also found to be saturated in respect to hydroxylapatite. Sequential extraction was used to determine the metal-bearing phases in the cave sediments and for discrimination of possible lithological and environmental effects. The mobility and bioavailability of the metals decrease approximately in the order of the extraction sequence. The operationally defined extraction sequence follows the order of decreasing solubility of the geochemical forms of the metals; hence the exchangeable fraction may indicate which metals are most mobile. The results of chemical sequential extraction analysis show that most of the Zn and Cu in cave sediments and the hydroxylapatite crusts are mainly controlled by the iron and manganese hydroxide (FEMN) and the organic fractions (OR) (Figs 3 & 4), the organic fraction plays an important role in sediment samples with direct influence of guano and in hydroxylapatite crusts while in samples with bone fragments the hydroxide control is dominant.

	Topsoil above the cave	Sediment with bone frag.	Sediment Below guano	Sediment with Guano
Depth	0-25cm	40-60cm	20-30cm	0-5cm
pH $_{H2O}$	6.07	6.36	6.77	3.19
SiO_2 %	40.12	55.26	44.88	35.45
Al_2O_3%	18.14	14.49	16.68	13.95
Fe_2O_3 %	7.21	6.06	6.2	5.54
MgO %	1.14	0.69	1.22	0.93
CaO %	2.36	5.79	9.43	16
Na_2O %	0.33	0.14	0.26	0.21
K_2O %	1.28	1.71	2.03	1.54
TiO_2 %	0.98	1.03	0.92	0.81
P_2O_5 %	0.31	5.51	3.36	5.84
MnO %	0.18	0.05	0.16	0.14
LOI %	27.8	9.1	14.7	19.4
Ctot %	7.63	0.19	1.3	3.28
Stot %	0.14	0.01	0.01	0.03
Co mg/kg	19.9	8.5	17	14.5
Rb mg/kg	98.6	90.7	123.2	95.6
Sr mg/kg	70	270	74	75
Th mg/kg	15.5	16.7	22.1	17.1
U mg/kg	3.2	5.8	5.9	7.4
V mg/kg	170	139	167	154
Cu mg/kg	32	63	62	165
Zn mg/kg	102	359	269	557
Ni mg/kg	57	25	53	41
Pb mg/kg	46	21	26	21
As mg/kg	28	16	22	20
Cd mg/kg	1.7	1.5	1.4	2.8
Sb mg/kg	0.5	0.7	1.2	1.3
Ba mg/kg	245	333	337	288

Table 1 Chemical composition of selected cave sediments and topsoil.

The residual (RES) fraction holds more than 45% of the total Zn content of the hydroxylapatite crusts indicating an incorporation of Zn into the crystal structure. Guano influenced sediments contain 5 to 10 % of Zn and Cu in the most mobile fractions the adsorbed (AD-less) and carbonate (CC-more). These the most liable fractions of elements in the case of pollution studies are used predict contamination usually of an anthropogenic source while in this case for influence on the quality of percolating cave waters.

Other potentially toxic elements (Pb, Cr, Ni, Co, As) analysed were found to have higher contents in topsoil and which are well within the regional geochemical baselines for Western Croatia (MIKO et al., 2000).

Although the primary goal of the study was to determine geochemical baseline values for the cave sediments and environment as well as possible influences from several decades of heavy traffic or war activities in the vicinity of Modrič cave the influence of bat guano as a natural contaminant obviously exceeds possible anthropogenic contributions.

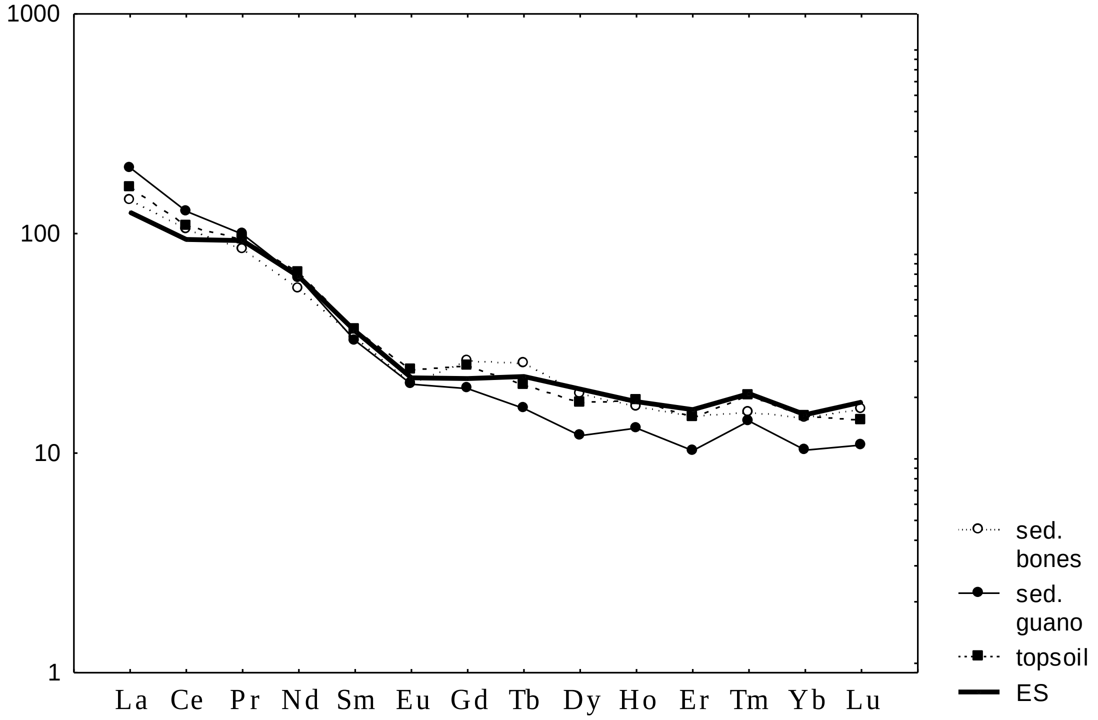

Fig. 2 Normalized REE patterns for cave sediments containing and those lacking guano, and topsoil, ES- European Shale.

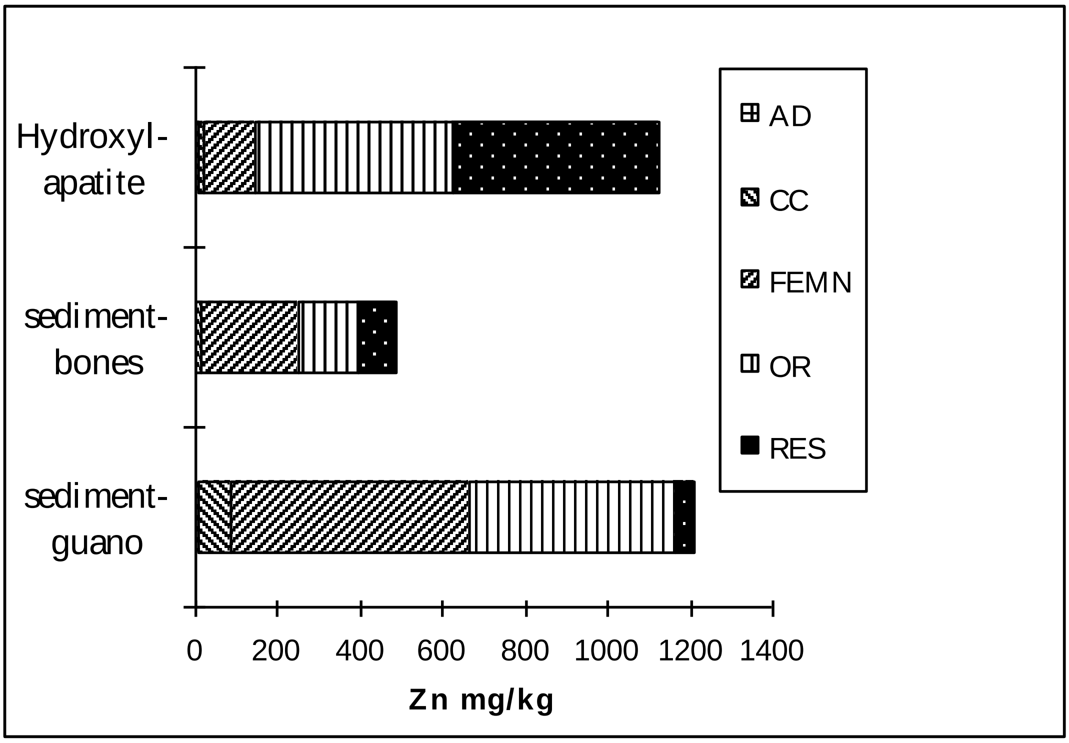

Fig. 3 Zinc concentrations in the cave sediment fractions, hydroxylapatite= hydroxylapatite crusts on flowstone.

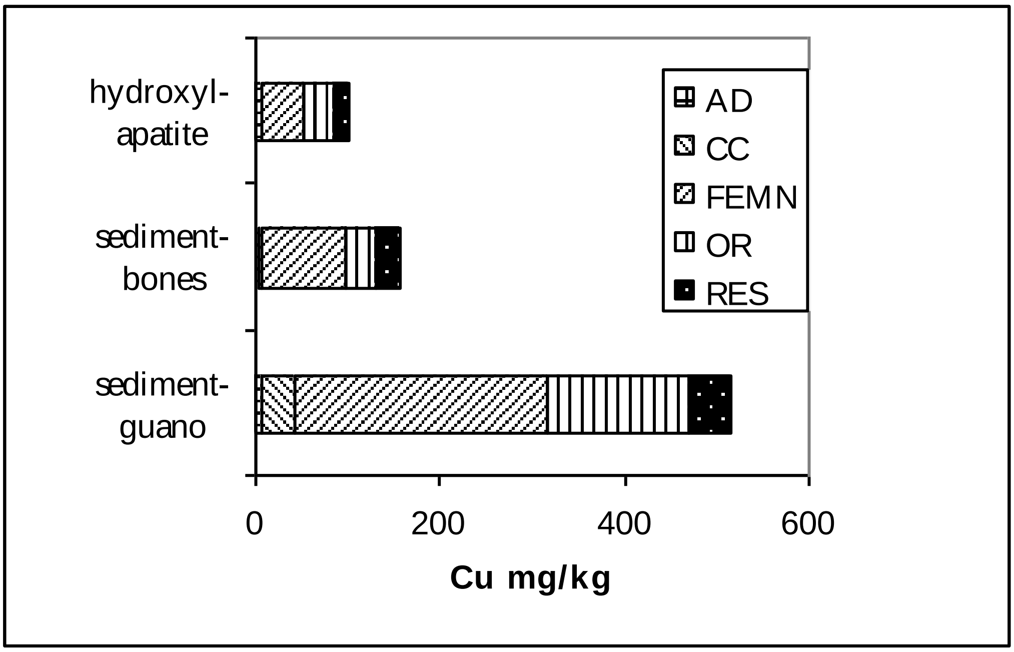

Fig. 4 Copper concentrations in the cave sediment fractions, hydroxylapatite= hydroxylapatite crusts on flowstone.

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