



New insight into geochemistry and mineralogy of speleothems in Croatian karst and its implications for paleoenvironmental reconstructions

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The Croatian karst is mostly situated in the Dinaric karst that it is worldwide known as the locus typicus of classical karst. Until recently, caves of Croatian karst were very poorly investigated in terms of their geochemistry and mineralogy. Therefore in 2016 a study was launched [1] with the aim to detect proxies from speleothems that are suitable for paleoenvironmental research. The main subject of our research was elemental composition and mineralogy of speleothems from various sites in Croatian karst and whether the different climatic, geological and hydrological characteristics affect elemental and mineralogical characteristics of speleothems. Total of 37 speleothem samples from 32 caves in different geological, geomorphological and climatic zones of Croatian karst were investigated. In all samples concentration of 30 elements was determined by ICP-MS and mineral composition was analyzed by XRD (identified minerals beside calcite were quartz, dolomite, muscovite/illite, chlorite and plagioclase). Besides the most abundant calcium, the elements with the highest concentrations (>500 mg/kg) were: Al, Fe, Si and Mg. A boxplot statistical method showed that largest numbers of anomalies were present in all three samples from Lukina jama located on Northern Velebit Mountain, where a whole series of elements show extreme values (Pb, Cu, Zn, Mn, Ni, Cr, Co, Ba, K, Mg, Li, Be, Al, U, Si, Ti, W, Fe, As).

As we found that most anomalies are present in the deep caves and pits of the Velebit Mt., we decided to launch a new study. The aim is to investigate changes of geochemical and mineralogical composition to the depth 1026 m in Slovačka jama pit and 1026 m in Cave system Velebita where intensive tectonics, especially during the Neotectonic period, with simultaneous and long lasting karstification, have resulted in an extremely complex structure of the karst system. Also sampling media was expanded, so that besides speleothems, sediment and rock samples and water chemistry were also investigated. Preliminary results have shown that most significant statistical anomalies of elements are present in the samples around possible paleochannel in Slovačka jama at the depth of 300-400 m. Factor analysis revealed that two main elemental associations of heavy metals exist – one of Fe, Pb, Cu and Zn, which come together with terrigenous elements Al, Si and Li, and the other elemental association of Cd, Cr, Mo and Ni, which might be of anthropogenic source. Mineralogical composition of samples from the new study is similar as from the first study, but some additional minerals like magnetite were found.

The study is still in progress and we hope that it will significantly contribute the knowledge about elemental and mineralogical composition of speleothems and cave sediments in Croatia, which are mostly determined by geogene influence.

[1] Paar, D., Frančišković-Bilinski, S., Buzjak, N. et al. (2016). *J. Geochem. Explor.*, 167, 20-37.