4.0.P02

Geochemical characteristics of miocene limestones of Tašmajdan and Kalemegdan (Belgrade, Serbia)

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In 1860 the saltpeter mine worked at Tašmajdan, in the centre of Belgrade, which was exploited, purified and later used for the gunpowder production. It was important reason for the investigation of underground cave at Tašmajdan and establishing the saltpeter origin. Petrology, mineralogy and geochemistry of the Miocene limestones of Tašmajdan were studied. They consist of allochems (fossil remains of algae, ooids), orthochems (sparry calcite) and terigenous compounds (quartz, feldspars).

The content of Ca, Mg, Na, K, Fe, nitrates, phosphates and some trace elements (Sr, Li, Ni, Cl) in bulk, water-soluble and HCl-soluble samples was analyzed. Limestones are characterized by increased content of nitrates of organic origin (up to 0.345 %). Comparing the content of nitrates with the contents of Ca, Mg and Na in a water-soluble part of sample it can be concluded that there is a polymineral agregate of Ca-, Mg- and Na-nitrate.

Contents of CaO (31.49-46.63 %), Ni (7-20 ppm) and Sr (470-640 ppm) correspond to the average values for carbonate rocks, while MgO (0.92-1.17 %), K_2O (0.06-0.13 %), Fe_2O_3 (0.17-0.25 %), Li (2-4 ppm) are lower than the average values. The content of Na is slightly higher than the average value and it is bonded for nitrates.

The Tašmajdan limestones and Kalemegdan ones represent unique reef barrier. In the oldest part of Belgrade, below the Kalemegdan fortress, limestones lie over sands of the same age. Limestones contain 0.021-3.478 % NO_3, 13-15 ppm Cu, 71-120 ppm Ni, 0.2-1.5 ppm Cr, 164-259 ppm Mn, 491-952 ppm Sr, 8-13 ppm Li, and 26-60 ppm Pb. Such enrichment in Pb can be explained by very intensive public trafic around fortress. A part of NO_3 probably is originated from gunpowder in many wars from the Middle Ages to XX century and from powder magazine located in these rocks.

4.0.P03

Migration of Rn and Pb in caves in the context of the U-Pb dating of speleothems of Quaternary age

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The U-Pb dating is gaining acceptance as a method potentially useful for dating speleothems of Quaternary age [e.g., 1]. Since the contents of U incoprorated in even the most U-rich speleothems are generally low (*ca*. n x 10 ppm), and the half-lives of U are large (4.47 x 10^9 yrs and 7.04 x 10^8 yrs for ^{238}U and ^{235}U, respectively) only tiny amounts of Pb could be generated *in situ* over Quaternary. It is critically important, thus, to use appropriate corrections for the radiogenic lead that was not formed *in situ*.

The "pool" of radiogenic Pb isotopes in a secondary mineral is commonly considered to comprise two parts: the "common Pb" brought about by mineral forming solutions and the *in situ* formed Pb. We point out that in case of the minerlas deposited in open cavities, there might be a third source of radiogenic Pb in a sample, which source can be described by the sequence: (1) decay of U in the bedrock and/or cave sediments; (2) diffusion migration of intermediate Rn isotopes into and within the cavity; (3) decay of Rn to Pb; (4) diffusion migration of Pb within a fluid filling cavity (air or water); (5) incorporation of Pb into the speleothem.

The latest step (incorporation of Pb) may take the form of the direct diffusion flux on the surface of the growing speleothem. Alternatively, it may take a more complex form of adsorption on and migration with cave aerosols.

Extensive studies have demonstrated that contents of Rn in caves range up to n x 10^4 Bk/m^3. Thus, the intensity of generation of radiogenic Pb inside caves might be significant. Although the chain of ^{235}U appear to be less susceptible to perturbations due to the fact that its intermediate ^{219}Rn is short-lived (3.96 s), our modeling shows that it may migrate via diffusion to a distance of ca. 1-2 mm from cave wall or sediment source. Distribution of ^{207}Pb born by decay of ^{219}Rn has calculated maximum within several mm from cavity wall. Thus, ^{207}Pb may be carried by flims of waters flowing over the cave walls and thus be incorporated in depositiong speleothems.

Although many processes mentioned above are difficult to quantify, researchers applying U-Pb method to dating speleothems of Quaternary age should be conscious of the possibility of the disturbance of the U-Pb system not only after but also before its closure.

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References

[1] Richards, D.A. et al. (1998) *GCA* **62** (23/24), 3683-3688.