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Preliminary geochemical investigation of karst barré from eastern Serbia Sokobanja basin

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Karst barré is a hydrogeological phenomenon which denotes a karst terrain of limited area completely surrounded by rocks of low permeability, i.e. whose lower part is enclosed and bordered by more or less impervious rocks impeding ground water flowing out of the karst area. Sokobanja basin is one of the first localities where this kind of karst was detected. This study represents a preliminary geochemical analysis of karst barré samples from this locality. Atomic absorption spectrometric analysis shows that the studied samples are composed predominantly of Ca and contain minor amounts of Mg, probably in form of carbonate minerals obtained by dissolving with mineral acids. There are no detailed geochemical data about karst barré from this or any other locality in the available literature to date.

Keywords: karst, karst barré, Sokobanja basin, geochemical analysis, AAS.

INTRODUCTION

Karst and karst barré. Karst is the term used to describe a special style of landscape containing caves and extensive underground water systems that is developed on particularly soluble rocks such as limestone, marble and gypsum [1]. Soluble rocks with extremely high primary porosity (~30-50%) usually have poorly developed karst. Karst barré denotes an isolated karst that is impounded by impermeable rocks. Stripe karst is a barré subtype where a narrow band of limestone, crops out in a dominantly clastic sequence, usually with a stratal dip that is very steep or vertical [2].

In Eastern Serbia karst belongs to the Carpatho-Balkanian geotectonic unit. It is characterized by isolated limestone areas separated by Neogene basins whose sediments cover the borders of the limestone areas. Some of the limestone masses are separated by Tertiary volcanic rocks. The thickness of limestone mass is not uniform, though the average thickness is 500 m. Karst is developed on mountain plateaus of various altitudes, starting from 500 to 700 m (on Miroč, Kalafat, Tresibaba Mts.), mostly situated at elevations from 1000 to 1100 m a.s.l. (at Beljanica, Devica, Ozren, Tupižnica, Vidlič, Tresibaba and Kučaj Mts.), and finally at 1500 - 1600 m a.s.l. (at Suva planina) [3].

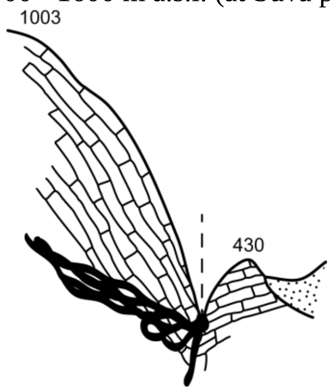

Fig. 1. Karst barré of the SB basin (based on Petrović and Petrović [4])

Soko Banja (SB) basin is the first locality on the Balkan peninsula where the karst barré (Fig. 1) has been detected by Cvijić [5]. This hydrogeological phenomenon can be recognised by lowering the spring under influence of groundwater which surrounds the karst. This phenomenon can represent a serious industrial problem with drinking water springs for water supply of population, considering the unpredictability of the spring.

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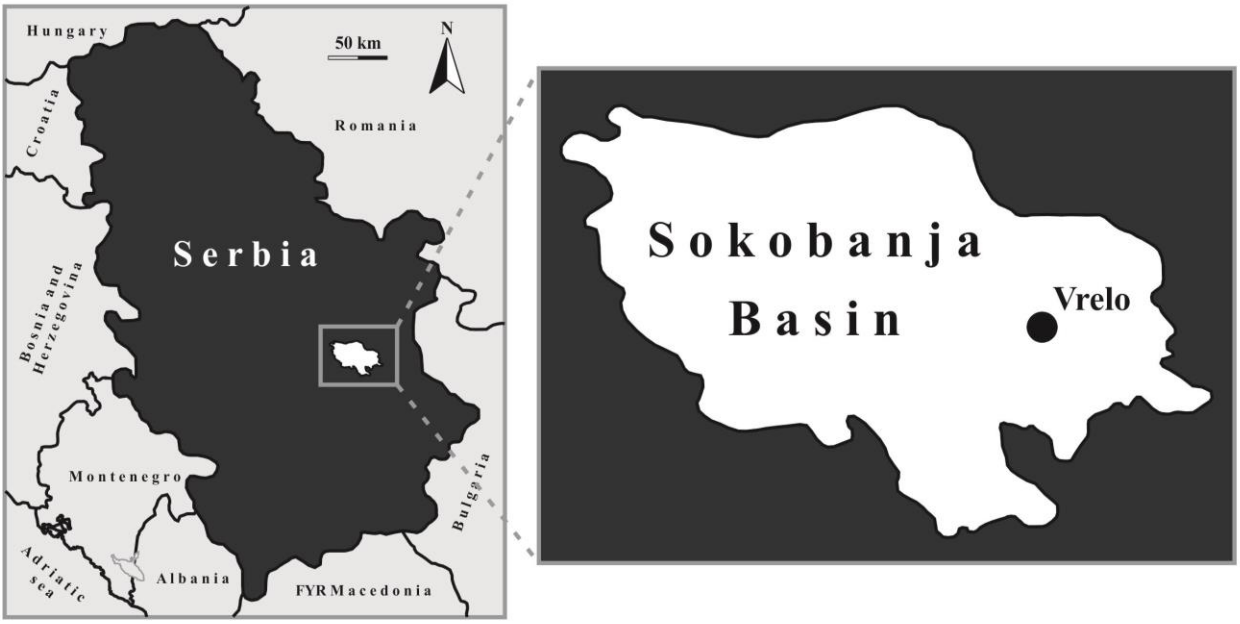


Fig. 2. Geographical location of SB basin

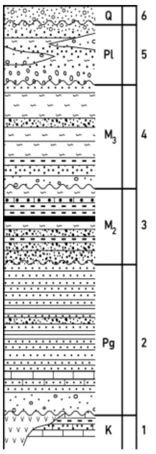
The aim of this preliminary study was to investigate the limestone facies and obtain more information of their geochemical composition.

Geographical location

The intermontane Sokobanja basin is located 250 km south-east of Belgrade (Fig. 1), and covers about 250 km^2. The Sokobanja basin is a north-south elongated tectonic depression with a maximum length of 29 km and width of 16 km. The basin was filled up by 1500 m thick limnic sediments, which had been accumulated during the time interval from the lower Palaeogene to the upper Miocene age [6,7]. The karst barré is most prominent at the east of the SB basin. The studied samples were collected from different locations of the SB (Fig. 2).

Geological setting

The complex tectonic evolution of the SB basin caused that it contains the rocks of various geological formations and compositions. The basement of the Sokobanja basin is composed of Proterozoic schist, Devonian schist and sandstone, Carboniferous schist and claystone with a thin coal bed, Permian sandstone, Triassic sandy limestone, Upper Jurassic dolomite and limestone, and Upper Cretaceous limestone (Fig 3) [8].



1. Upper Cretaceous; pyroclastic rocks,
2. Paleogene,
3. Middle Miocene (freshwater Čitkut coal-bearing series),
4. Panonnian stage (freshwater Vrmdžan coal-bearing series),
5. Pliocene series,
6. Quaternary

Fig. 3. Lithostratigraphic column of the SB basin (based on the Geological annals of the Balkan Peninsula [9])

These are mostly sedimentary formations, followed by crystalline shale and volcanic rocks, whose age is estimated at more than a billion years. Low-metamorphic Proterozoic shale of Bukovik and Rožanj formed the western rim of the basin, as well as the basal Tertiary sediments (Fig. 4, 5). The Carboniferous formations in the southern part of the basin are represented by conglomerates, quartz sandstones and shales with thin layers of coal. The Permian red sandstone, bedded limestones and dolomites are most common in the western part of the basin.

Eastern, northern and southern edges of the SB basin are mainly built of sediments of the Mesozoic age. The mountain massifs of Rtanj, Krastatac, Devica, Ozren and Leskovik are built of upper

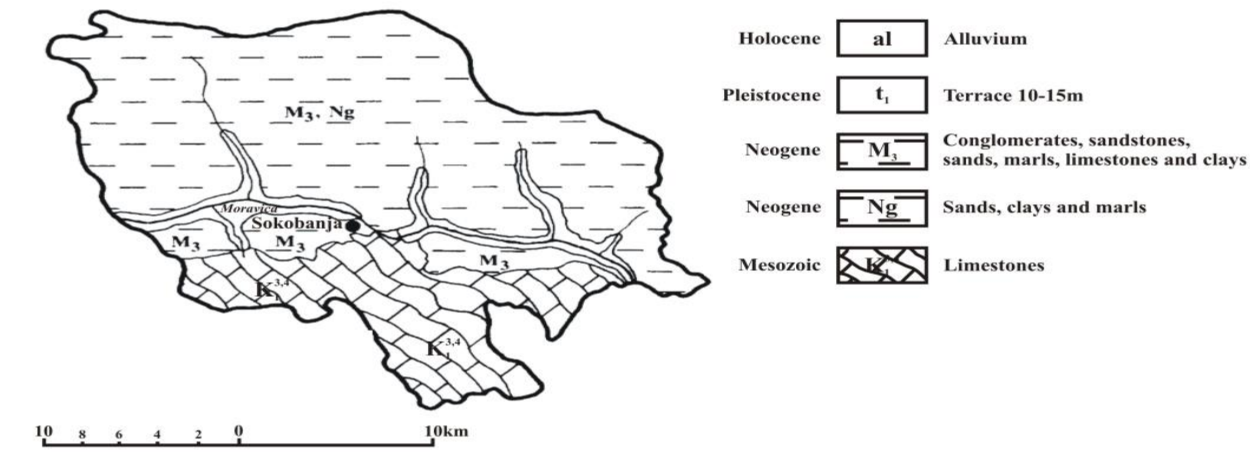


Fig. 4. Geological map of the SB basin (based on the Geological Guide [10])

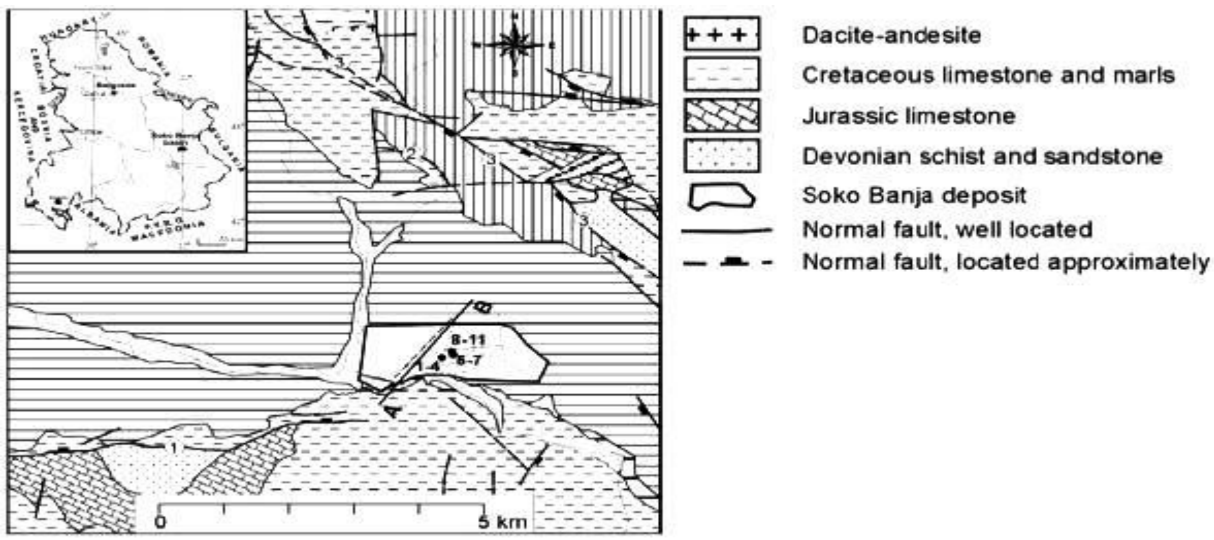


Fig. 5. Simplified tectonic map of the Soko Banja basin (modified after the Basic Geologic Map of the SFRY (modified after Novković et al. [6]).

Jurassic oolitic laminar and stratified limestone and dolomite. Four series [6] of sediments are recognized:

1. The Lower Palaeogene Series
2. The Čitluk Series
3. The Vrmdža Series
4. The Upper Series

The most important Soko Banja, Vrmdža, and Rtanj-Krstatac faults strike E–W, WNW–ESE, NW–SE, respectively [7]. There are also minor faults running N–S, which, together with the previously mentioned, control both the general contour and the shape of the basin.

EXPERIMENTAL

Six samples of karst barré from Sokobanja valley were investigated. (Fig. 1) Samples were collected from the surface of the SB. Three samples were collected from Vrelo locality (43° 38' 03"N, 21° 59' 57"E) (samples 1, 2 and 3). The other samples were collected from the flow of the river Moravica (4,5,6).

Fractionation procedure

Pre-treatment. Before treatment with mineral acids, the samples were grinded in a vibrating mill to a particle size of 100 μm. The fractionation procedure was similar to that used by Premović *et al*. [11]. The flow chart in Fig. 6 outlines the major steps in preparing the two fractions of samples from SB basin.

Dissolution in acetate buffer. The powdered sample (1 g) was added in small amounts to 25 mL of 1 M acetate buffer (CH_3COOH/CH_3COONa, pH 4.8). After that the solution was mixed on a magnetic stirrer, without heat, for 12 h, then centrifuged and rinsed with distilled water to a negative reaction to acetate. The residue was dried in an electric oven at 105 °C and weighed. The difference between the masses of untreated sample and insoluble residue, equals the percentage of fractions soluble in acetate buffer. The soluble material constitutes the carbonate fraction.

Dissolution in hydrochloric acid. The insoluble residue was further demineralized by repeated treatment with cold 6 M HCl. This acid solution removed most of the metal oxides. After rinsing and drying, the remainder was weighed and the fractions soluble in cold HCl were determined. The soluble material constitutes the fraction of metal oxides and hardly soluble carbonates.

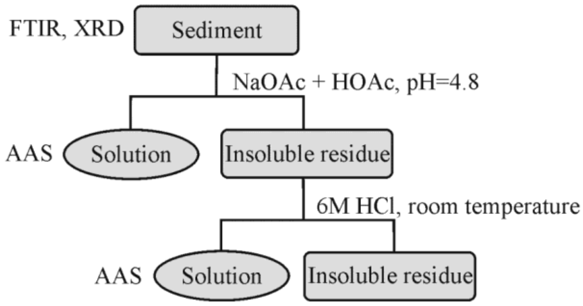


Fig 6. Flow chart of fractionation procedure

X-ray powder diffraction (XRPD) analysis

XRD analyses of the whole sample and the carbonate-free fraction were performed using a powder diffractometer SIEMENS D500 equipped with a scintillation counter, using Ni-filtered Cu radiation (λ = 1.54184 Å) at 35 kV and 20 mA. The diffractograms of the samples were recorded in the range from 4 to 75° 2θ with 0.02° step and retention time of 0.5 s at each step. Program Search/Match was used for comparison of the diffractograms of the recorded samples to a database for identification of the crystalline phases in the samples. Analyses were performed in the Laboratory for Materials (Institute of Nuclear Sciences, Vinča).

Fourier Transform Infrared (FTIR) spectroscopy

The functional groups available in the untreated samples were detected by the KBr technique using FTIR spectroscopy (Bomem, Hartman & Braun MB-100 spectrometer). The spectra were recorded at room temperature in the range from 4000 to 400 cm^{-1}. The KBr pellets were prepared from 1.5 mg finely powdered samples dispersed in 150 mg of anhydrous KBr. The obtained FTIR spectra were analyzed using Win Bomem Easy software. FTIR analyses of whole samples were performed in the Spectroscopy Laboratory (Faculty of Technology, Leskovac).

Atomic absorption spectrometry (AAS) analysis

The concentrations of metal ions (Ca, Mg and Fe) in the soluble residues were determined on a flame atomic absorption spectrometer Varian Spectra A-20 (Mulgrave, Victoria, Australia). Analyses were performed in the Laboratory for Applied and Industrial Chemistry (Faculty of Science, University of Niš).

RESULTS AND DISCUSSION

Sequential demineralization analysis showed that karst barré samples from the SB basin are completely dissolved after treating with acetate buffer (55.20 % of the sediment) and cold HCl (44.80 %) implying the absence of clay and other silicate minerals, as well as organic matter.

A typical FTIR spectrum of untreated sample is shown in Fig. 7. Similar spectra were recorded for all studied samples with bands characteristic for calcite and no bands that would indicate the presence of some other mineral phases. The carbonates in the samples were confirmed by the strong absorption bands between 3050-2850 cm^{-1}, 2650-2500 cm^{-1}, 1500-1400 cm^{-1}, and at 1800 cm^{-1}, 878 cm^{-1}, and 714 cm^{-1} (Fig. 7, Table 1). Dolomite displays characteristic FTIR absorption bands at 3020 cm^{-1}, 2626 cm^{-1} and 730 cm^{-1}, and the presence of these bands would indicate the presence of this mineral. However, the spectra of the investigated samples showed no presence of dolomite, probably owing to the low content of this mineral.

Table 1. Assignment of absorption bands to characteristic vibrations in theFTIR spectra of karst barré samples

Assignment	Sample Wavenumber (cm^{-1})	Mineral type
ν(OH) stretching	2514	Calcite
ν(C=O) stretching	1800	Calcite
$\nu_3(CO_3^{2-})$ asymm. stretching	1426	Calcite
$\nu_2(CO_3^{2-})$ out-of-plane	878	Calcite
$\nu_4(CO_3^{2-})$ planar stretching	714	Calcite

The X-ray diffraction analysis made it possible to identify the main crystalline phases in the studied samples. According to the interplanar distance values characteristic for each crystal, only one mineral has been found, calcite ($CaCO_3$), Figs. 8a/b. The chemical analysis of each sample (Table 2) showed that the studied samples also contain Mg carbonate, probably in form of dolomite, but the crystalline phases for this mineral were not identified due to the low content of this mineral in all studied samples.By AAS analysis only Ca^{2+}, Mg^{2+} and Fe^{3+} ions (in form of oxides in Table 2) were detected in the solutions after dissolution with mineral acids. The se metals are probably present as carbonate minerals in the sample.

Table 2. Results of the geochemical analysis of karst barré samples from the SB basin.

	Acetate buffer [wt %]	**Cold HCl [wt %]**
Solubility	54.8-55.4	44.6-45.2
CaO	48.3-53.6	35.8-39.4
MgO	2.7-4.0	0.9-2.4
Fe_2O_3	/	0-0.1

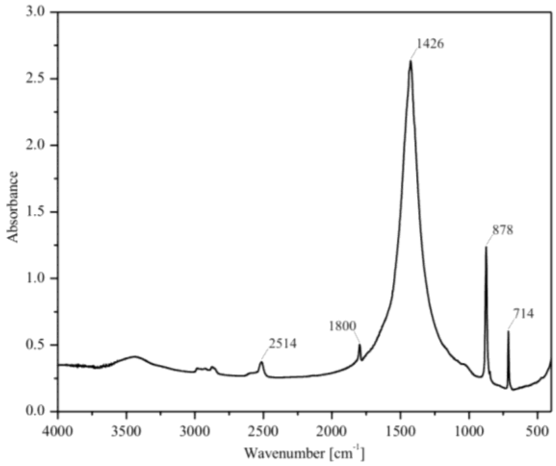


Fig. 7. FTIR spectrum of untreated sample

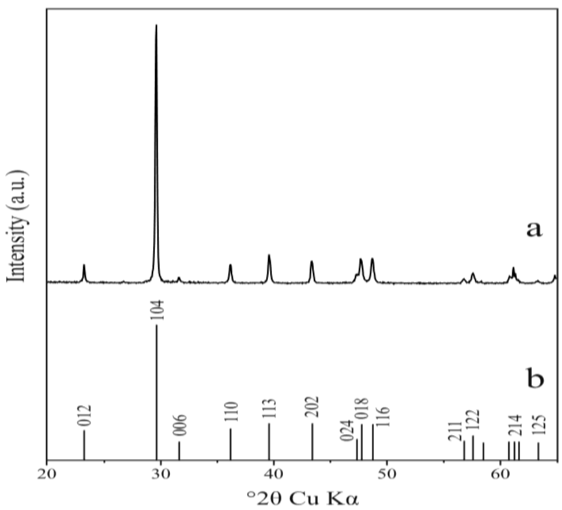


Fig. 8. a) XRPD patterns of untreated sample; (b) standard diffraction pattern for calcite (JCPDS card No. 83-0578).

The stereo-microphotographs of fine-grained raw (Fig. 9a) and acetate buffer treated (Fig. 9b) karst barré samples show that the material is homogenous calcite with no presence of organic matter and non-carbonate minerals.

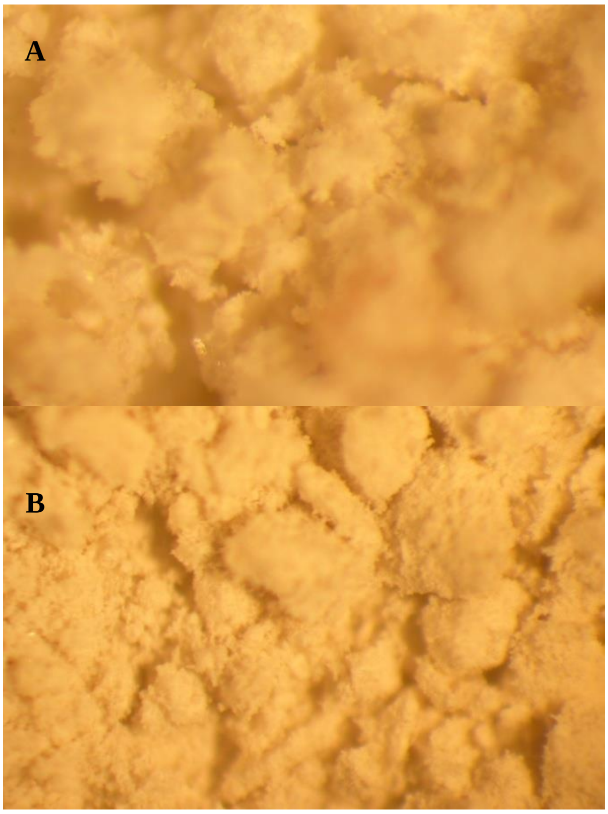


Fig. 9. Stereo-microphotographs (magnification up to 180×) of A) raw sample, and B) acetate buffer treated sample from SB basin.

CONCLUSION

Sokobanja basin is the first locality where karst barré has been detected. Karst barré as a hydrogeological phenomenon can be recognised by lowering the spring under influence of groundwater which surrounds the karst. This phenomenon can present serious problems with springs for municipal drinking water supply, considering the unpredictability of the spring behaviour.

The mineralogical analyses by XRD and FTIR techniques imply that the investigated samples are composed of pure calcite. Other mineral phases are not detected (probably because their contents are below the detection limits). The results of sequential demineralization procedure and atomic absorption spectrometric analysis show that the studied samples are composed predominantly from $CaCO_3$ and contain minor amounts of $MgCO_3$/$CaMg(CO_3)_2$, which is in correspondence with the chemical composition of karst. No clay, other silicate minerals, or organic matter were detected in the samples. The hydrogeological phenomenon that accompanies the karst confirmed the assumption that the samples from the investigated locality belong to the karst barré.

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ПРЕДВАРИТЕЛНО ГЕОХИМИЧНО ИЗСЛЕДВАНЕ НА КАРСТОВА КОТЛОВИНА В БАСЕЙНА НА СОКОБАНЯ В ИЗТОЧНА СЪРБИЯ

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(Резюме)

Карстовите котловини (karst barré) са хидрогеологично явление, което се характеризира с ограничен карстов терен, заобиколен от скали с ниска пропускливост (ниските им части са ограничени от непроницаеми скали, пречещи на изтичането на подземните води). Басейнът Сокобаня е едно от първите места, където са открити такива карстови образувания. Това изследване представя предварителен геохимичен анализ на проби от това място. Анализът с атомно-абсорбционна спектрофотометрия показва, че изследваните проби са съставени главно от калций и съдържат малки количества от магнезий, вероятно като карбонати. Досега не са известни подробни геохимични данни за такива обекти на други места.