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#### A review of Pb-Sb(As)-S, Cu(Ag)-Fe(Zn)-Sb(As)-S, Ag(Pb)-Bi(Sb)-S and Pb-Bi-S(Te) sulfosalt systems from the Boranja orefield, West Serbia

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Abstract. Recent mineralogical, chemical, physical, and crystallographic investigations of the Boranja orefield showed very complex mineral associations and assemblages where sulfosalts have significant role. The sulfosalts of the Boranja orefield can be divided in four main groups: (i) Pb-Sb(As)-S system with  $\pm$ Fe and  $\pm$ Cu; (ii) Cu(Ag)-Fe(Zn)-Sb(As)-S system; (iii) Ag(Pb)-Bi(Sb)-S; (iv) and Pb-Bi-S(Te) system. Spatially, these sulfosalts are widely spread, however, they are the most abundant in the following polymetallic deposits and ore zones: Cu(Bi)-FeS Kram-Mlakva; Pb(Ag)-Zn-FeS<sub>2</sub> Veliki Majdan (Kolarica–Centralni revir–Kojići); Sb-Zn-Pb-As Rujevac; and Pb-Zn-FeS<sub>2</sub>-BaSO<sub>4</sub> Bobija. The multi stage formation of minerals, from skarnhydrothermal to complex hydrothermal with various stages and sub-stages has been determined. All hydrothermal stages and sub-stages of various polymetallic deposits and ore zones within the Boranja orefield are followed by a variety of sulfosalts.

Key words: Sulfosalts, Boranja orefield, West Serbia.

Апстракт. Досадашња минералошка, хемијска, геохемијска и кристалографска проучавања показала су да се у рудном пољу Борање јављају веома сложене минералне асоцијације и парагенезе, где у њеним полиметаличним минерализацијама доминирају минерали из групе сулфосоли. Сулфосоли из рудног поља Борање могу се поделити у четири веће групе: (i) систем Pb-Sb(As)-S, са ±Fe и ±Cu; (ii) систем Cu(Ag)-Fe(Zn)-Sb(As)-S; (iii) систем Ag(Pb)-Bi(Sb)-S; (iv) систем Pb-Bi-S(Te). Ове сулфосоли су просторно веома распрострањене, међутим, оне су најзаступљеније у следећим полиметаличним лежиштима и рудним зонама: Cu(Bi)-FeS Крам–Млаква; Pb(Ag)-Zn-FeS<sub>2</sub> Велики Мајдан (Коларица–Централни ревир–Којићи); Sb-Zn-Pb-As Pyjeвац; Pb-Zn-FeS<sub>2</sub>-BaSO<sub>4</sub> Бобија. Утврђено је вишеетапно стварање минерала, где прва одговара скарн-хидротермалном а друга сложеном хидротермалном, са већим бројем стадијума и подстадијума. Сви стадијуми и подстадијуми хидротермалне етапе у минералним асоцијацијама различитих полиметаличних лежишта и рудних зона, праћени су појавом широке лепезе сулфосолних минерала.

#### Introduction

Sulfosalts are complex sulfide minerals with the general formula:  $A_m B_n S_p$ ; where A represents a metal such as Cu, Pb, Ag, Fe and rarely Hg, Zn, V; B usual-

ly represents semi-metal such as As, Sb, Bi and rarely Ge, or metals like Sn and rarely In; and S is S or rarely Se or/and Te (ANTHONY *et al.* 1990; MOËLO *et al.* 2008). Formerly, it was believed that the sulfosalts were salts of complex hypothetical thioantimonic or

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thioarsenic acids (e.g.,  $HSbS_2$ ,  $H_{18}As_4S_{15}$ ,  $H_3AsS_3$ ). X-ray diffraction (XRD) analyses indicate that the crystal structures of Pb-Sb-As-S sulfosalts are based on structural fragments of simpler compounds such as galena (lead sulfide; PbS) blocks and stibnite (antimony trisulfide; Sb<sub>2</sub>S<sub>3</sub>) sheets (WERNICK 1960). No encompassing theory has been evolved to rationalize many of these curious compounds. The complexity of many of the structures evidently results from them having crystallized at low temperatures and the consequent high degree of ordering of the metal atoms. Syntheses of such compositions at higher temperature usually result in structures simpler than the complicated low-temperature forms. There are about 200 known sulfosalts (MOËLO *et al.* 2008).

These minerals were formed under the mutual influence of different sulfantimonide, sulfarsenide, sulfstanate, sulfbismuthinide, etc. anions (e.g. SbS<sub>2</sub><sup>1-</sup>, As<sub>4</sub>S<sub>15</sub><sup>18–</sup>, AsS<sub>3</sub><sup>3–</sup>, Bi<sub>2</sub>S<sub>6</sub><sup>6–</sup>), with metal ions (e.g., Cu<sup>1+;</sup> <sup>2+</sup>, Ag<sup>1+</sup>, Fe<sup>2+</sup>, Pb<sup>2+</sup>). These reactions occur only in mineralized solutions with increased alkalinity and high concentration of H<sub>2</sub>S. Deposition of miargirite AgSbS<sub>2</sub>, pyrargyrite Ag<sub>3</sub>SbS<sub>3</sub> and stephanite Ag<sub>5</sub>SbS<sub>3</sub> occur during mutual influence of sulfantimonide anions with Ag<sup>1+</sup>. Interactions between already deposited sulfides (galena, chalcopyrite, etc.) and mineralized solutions (ascendant and/or descendent) may result in the formation of younger sulfosalts. The typical example of the reaction crystallization is contact between galenachalcopyrite with sulfantimonide solutions when bournonite PbCuSbS<sub>3</sub> was deposited. The corrosive reaction is characteristic for influence of sulfantimonide solutions along galena surfaces thus creating wool-like variety boulangerite  $Pb_4Sb_3S_{11}$  and/or semseyite  $Pb_9Sb_8S_{21}$ (RAMDOHR 1980; ANTHONY et al. 1990). Moreover, decrease of temperature and pressure led to decomposition of high-temperature solid solutions when two or more stable sulfosalts phases were formed. This is particularly visible in Pb-Ag-bearing sulfbismuthinide when complex exsolutions with lamellae structures were deposited (i.e., phases along the lillianite-gustavite solid solution Pb<sub>3</sub>Bi<sub>2</sub>S<sub>6</sub>-AgPbBi<sub>3</sub>S<sub>6</sub>) (COOK 1997).

Although under exceptional circumstances some sulfosalts may constitute Ag ores (i.e., proustite, pyrargyrite, and stephanite), and other species have constituted Ag ores (in minor amounts), Hg, Tl, As, and Sb (i.e., boulangerite, livingstonite, enargite, and tennantite-tetrahedrite groups), their economic importance is sometimes significant (Ag in the Pb-concentrate) and sometimes trivial. Aside from mineralogical curiosities, the sulfosalts are of interest because their electronic properties are related to those of semiconductors (CHVILYOVA *et al.* 1988).

The Boranja orefield (BOF) is well-known since the Roman Empire and Medieval times and is still important factor of modern mining in this part of Serbia. Significant research began during the second half of the 20<sup>th</sup> century. Comprehensive mineralogical, crystallographic, geochemical and petrological studies yielded important results in defining mineral compositions of the mineralizations and surrounding rocks (e.g. KARAMATA 1955; RADUKIĆ 1960; TOMIĆ 1962; BORODAEV 1978; JANKOVIĆ 1978; RADOSAVLJEVIĆ *et al.* 1982). This study shows a synthesis of previous research of sulfosalts with revisited and new data.

#### Materials and methods of study

Polished sections were prepared for reflected-light microscopy and Electron Probe Micro–analyses (EPMA), following standard preparation and polishing steps (PICOT & JOHAN 1982). The Carl-Zeiss polarizing microscope, model JENAPOL-U equipped with 10×, 20×, 50×, 100× (oil immersion) objectives and a system for a photomicrography ("Axiocam 105 color" camera and "Carl Zeiss AxioVision SE64 Rel. 4.9.1." software package with "Multiphase" module).

EPMA were performed on a JEOL JSM-6610LV scanning electron microscope (SEM) connected with an INCA energy-dispersion X-ray analysis unit; EDX analytical system. An acceleration voltage of 20 kV was used. The samples were coated with gold. The following standards and analytical lines were used: FeS<sub>2</sub> (FeKa, SKa), ZnS (ZnKa, SKa), Mn (MnKa), Ni (NiKa), Co (CoKa), Cu (CuKa), InAs (AsKa,), InSb (SbLa), SnO<sub>2</sub> (SnLa), Ag<sub>2</sub>Te (AgLa), CdS (CdLa), HgS (HgMa), PbS (PbMa), and Bi (BiMa). EDX detection limits were  $2\sigma \sim 0.3$  wt% (counting time 60 sec). General formulae were calculated according to ANTHONY *et al.* (1990).

#### **Occurrence and geological settings**

The Podrinje metallogenic district (PMD) belongs to the Serbo-Macedonian Metallogenic Province (SMMP) and includes several smaller orefields: Boranja (Serbia), Cer (Serbia), and Srebrenica (Bosnia and Herzegovina) (VANĐEL 1978; JANKOVIĆ 1990). The Boranja orefield (BOF) covers an area of about 200 km<sup>2</sup>. It is situated on the SE margin of the Oligocene granodiorite pluton of Boranja (DELALOYE *et al.* 1989; STEIGER *et al.* 1989), which belongs to the Dinaridic granitoid suite of the Late Paleogene – Early Neogene age (CVETKOVIĆ *et al.* 2000), and is situated on a border of three terranes – the Jadar block terrane (FILI-POVIĆ 2005), the Vardar zone composite terrane and the Drina–Ivanjica terrane (KARAMATA & KRSTIĆ 1996; KARAMATA *et al.* 1997).

It consists of Paleozoic, Mesozoic, and Tertiary formations (Fig. 1). Paleozoic is represented by Carboniferous sediments, mostly slates and sandstones of low-grade metamorphism, and limestones ("the Drina series"). Mesozoic complex consists of Triassic, Jurassic and Cretaceous formations, mostly slates, limestones, volcanic sediments, basic and ultrabasic rocks (SIMIĆ 1957; ĐOKOVIĆ 1985; NEUBAUER 2002).

Mineralization of the BOF is concentrically distributed around the Tertiary granodiorite of Boranja (Fig. 1). Around the intrusion, in the skarn alteration halo, several small Fe deposits occur (magnetite and pyrrhotite), and less frequently Bi, W and Mo deposits (Velika Reka, Vranovac). The Cu(Bi)-FeS Kram-Mlakva ore zone belongs to small Cu polymetallic skarn deposits (Fig. 1). Outwards the granodiorite, the Pb(Ag)-Zn Veliki Majdan ore zone consists of ore bodies embedded in carbonates on the contact with quartz latite and Paleozoic slates (Fig. 1). The main mineral association includes pyrrhotite, pyrite, sphalerite, galena, chalcopyrite, and Pb(Ag)-Sb sulfosalts in lesser amounts (ČIKIN *et al.* 1983). The outermost halo hosts several Sb deposits (Fig. 1). The most important are situated in the Brasina–Zajača–Stolice–Dobri potok intrusive-volcanic zone with the following leading ore elements Sb, Pb, Zn, Fe, Ba, and F; in the Rujevac–Crvene stene–Vujanoviča–Brezovica volcanogenic-sedimentary zone of Diabase-Chert Formation (DCF) with the following metals: Sb, Pb, Zn, Fe, As, Ba, and Hg. The ore bodies occur as irregular pipes and lenses in silicified Carboniferous limestones (BORODAEV 1978; JANKO-VIĆ 1979; ĐURIČKOVIĆ 2005).

Minerals of the BOF were deposited in several successive stages, which together correspond to a single regional-scale mineralization event that is related to the subvolcanic-plutonic intrusions of the Boranja magmatic complex. This is well demonstrated by the



Fig. 1. Detailed geological and metallogenic map of the BOF (modified according to Basic Geological Map of Serbia, 1:100,000). Upper left corner shows exact location of BOF within Serbia (MONTHEL *et al.* 2002).

zonal arrangement of several metallic mineral associations (Fe-Cu(Bi) $\rightarrow$  Pb(Ag)-Zn $\rightarrow$  Sb(As)-Pb-Zn $\rightarrow$ CaF<sub>2</sub>(Pb-Zn), with increasing distance from the Boranja granodiorite (RADOSAVLJEVIĆ *et al.* 2013A).

The Bobija polymetallic barite-sulfide deposit is situated in East slopes of Sokolske Mnt., which is some 15 km to the NE away from Ljubovija. The deposit itself consists of complex geological composition mainly built of Paleozoic and Mesozoic sediments (JANKOVIĆ 1990). The Bobija deposit is composed of massive barite and sulfide FeS<sub>2</sub>-Pb-Zn-Cu elongated lens-like ore bodies. Massive barite ore bodies are consisted of 50 to 90 wt% of BaSO<sub>4</sub> (RADO-SAVLJEVIĆ *et al.* 2013B).

#### **Mineralogy of sulfosalts**

The sulfosalts of the BOF can be divided in the four main groups: (i) Pb-Sb(As)-S system, with  $\pm$ Fe and ±Cu-zinkenite, fülöppite, plagionite, robinsonite, boulangerite, jamesonite, bournonite, twinnite, geocronite and gratonite; (ii) Cu(Ag)-Fe(Zn)-Sb(As)-S system – tetrahedrite, tennantite, and Ag-bearing tetrahedrite; (iii) Ag(Pb)-Bi(Sb)-S system – pyrargyrite, diaphorite, freieslebenite, Sb-bearing schirmerite, Ag-bearing nuffieldite, and fizélvite; (iv) Pb-Bi-S(Te) system - bursaite, cannizzarite, cosalite, aikinite, ustarasite, and tetradymite. Spatially, these sulfosalts are widely spread, but they are most abundant in the following polymetallic deposits and ore zone: Cu(Bi)-FeS Kram-Mlakva, Pb(Ag)-Zn-FeS<sub>2</sub> Veliki Majdan (Kolarica-Centralni revir-Kojići), Sb-Zn-Pb-As Rujevac, and Pb-Zn-FeS<sub>2</sub>-BaSO<sub>4</sub> Bobija (Fig. 1). Most of them are lead gray with a metallic luster, brittle and difficult to distinguish without using XRD method and Electron Microprobe analyses (EPMA).

Their mutual structural and textural characteristics are complex, and characterized by small grain size ( $\leq$ 5–100 µm), which beside intergrowths (effects of reaction and/or corrosive processes, high-temperature exsolution products, etc.) additionally makes it difficult to single it out for crystallographic (XRD) and chemical (spectrochemical and mass spectrometric) investigations. Chemical composition of the minerals was calculated according to ANTHONY *et al.* 1990. Besides so far determined sulfosalts, new minerals from the Pb-Ag-Bi-Sb-S system could be discovered (RADOSAVLJEVIĆ 1988).

#### Sulfosalts of the Pb-Sb(As)-S system, with ±Fe and ±Cu

This sulfosalt group is most abundant occurring in almost all deposits and mineralizations of the Boranja orefield. Sulfosalts of Pb-Sb(As) composition are the most common in the Rujevac polymetallic Sb-Zn-PbAs deposit. In this deposit Pb was characteristically deposited after Sb (BORODAEV 1978), which genetically deviates from other Sb deposits and occurrences within the SMMP. There are various of sulfosalts belonging to the sphalerite-Pb-Sb(As) sulfosalt-As mineral assemblage, which are very dominant. So far, the following sulfosalts have been determined: *zinkenite* – Pb<sub>8,93</sub>(Sb<sub>18.94</sub>,As<sub>3.08</sub>)<sub>222.02</sub>S<sub>42.02</sub>; *fülöppite* – Pb<sub>2.86</sub>(Sb<sub>7.01</sub>,As<sub>1.07</sub>)<sub>28.08</sub>S<sub>15.06</sub>; *plagionite* – Pb<sub>4.97</sub> (Sb<sub>7.29</sub>, As<sub>0.76</sub>)<sub>28.02</sub>S<sub>17.00</sub>; *robinsonite* (?); *twinnite* – Pb<sub>0.97</sub>(Sb<sub>1.42</sub>,As<sub>0.60</sub>)<sub>22.02</sub>S<sub>4.00</sub>; and *gratonite* (determined only microscopically, RADOSAVLJEVIĆ 1988; 2012).

The most abundant sulfosalt of the sphalerite-Pb-Sb(As) sulfosalt-As mineral assemblage is zinkenite. It was first discovered by JANKOVIĆ et al. (1977) and MOËLO et al. (1983), and later supplemented by new data by RADOSAVLJEVIĆ (1988), ZARIĆ et al. (1992), RADOSAVLJEVIĆ (2012), RADOSAVLJEVIĆ et al. (2012), and RADOSAVLJEVIĆ et al. (2014a). It occurs in the following mineral association: Pb-Sb(As) sulfosalts, sphalerite, arsenopyrite, realgar, duranusite, native As, stibarsen, dolomite, and quartz. It occurs as tabular, needle- and wool-like fibrous individuals (plumosite), forming larger individual aggregates mostly in the interstices of the quartz matrix. Its central zones are locally replaced by plagionite. Moreover, zinkenite intensively intersects, penetrates and overgrowths cataclased sphalerite aggregates (Fig. 2f). It also contains inclusions of quartz and duranusite. When replacing crystal aggregates of older stibnite, it is often penetrated and overgrown along its edges by dolomite metacrysts. Twinnite is characterized by polysynthetic twinning and commonly occurs as the youngest sulfosalt along the edges of stibnite, lesser plagionite. Although it is mentioned in the literature (JANKOVIĆ et al. 1977), robinsonite was not confirmed in our study. In addition, according to PRUSETH et al. (1997), robinsonite is unstable at temperatures below 300 °C, confirming its absence in this deposit.

Besides major elements, EPMA of sulfosalts usually show presence of As (up to 8.00 wt%), Ag (up to 0.04 wt%), Cu (up to 0.03 wt%) and Fe (up to 0.01 wt%). Hg, Zn, Cd, Bi and Tl were not detected (RADOSAVLJEVIĆ 2012).

Pb-Sb(As) sulfosalts, associated to the Veliki Majdan ore zone, include: *jamesonite* – Pb<sub>3.99</sub>(Fe<sub>1.00</sub>, Cu<sub>0.01</sub>)<sub> $\Sigma$ 1.01</sub>Sb<sub>6.00</sub>S<sub>14.00</sub>; *boulangerite* – Pb<sub>5.02</sub>Sb<sub>4.15</sub> S<sub>10.83</sub>; *geocronite* – Pb<sub>14.21</sub>(Sb<sub>3.05</sub>,As<sub>2.74</sub>)<sub> $\Sigma$ 5.79</sub>S<sub>23.00</sub> (Fig 2a); *bournonite* – Pb<sub>1.00</sub>Cu<sub>1.00</sub>(Sb<sub>0.94</sub>,As<sub>0.06</sub>)<sub> $\Sigma$ 1.00</sub> S<sub>3.00</sub>; *As-bournonite* – Pb<sub>1.00</sub>(Cu<sub>0.97</sub>,Fe<sub>0.02</sub>)<sub> $\Sigma$ 0.99</sub>(Sb<sub>0.54</sub>, As<sub>0.48</sub>)<sub> $\Sigma$ 1.02</sub>S<sub>2.99</sub>; and accompanying the pyrite-galenasphalerite mineral assemblage (DIMITRIJEVIĆ & RAKIĆ 1978; RAKIĆ *et al.* 1984; RADOSAVLJEVIĆ *et al.* 1993; RADOSAVLJEVIĆ *et al.* 2013a).

The most abundant sulfosalt of the Veliki Majdan ore zone is jamesonite. It occurs as short-prismatic crystals, deposited in the interspaces of chalcopyrite and calcite aggregates. Bournonite most frequently occurs at the grain boundaries between galena and chalcopyrite replacing galena (Fig. 2b). It is Ag-free, and contains As from 0.5 to 7.7 wt%. As-bearing bournonite also occurs in the epithermal Au-Te vein system of the Sacarimb deposit in Romania (CIOBANU *et al.* 2005). EPMA data yielded stoichiometric composition, without presence of any other element except As.

Besides these Pb-Sb sulfosalts, new analyses confirmed presence of a Sb-member with the highest Sb content (46.4–46.7 wt%) in the Centralni revir locality within the Veliki Majdan ore zone. EPMA yielded following average crystallochemical formula of fülöppite  $Pb_{3.02}Sb_{7.97}S_{15.01}$  (3 analyses). It is deposited in interspaces between pyrite grains in short prismatic forms (Fig. 2c). Unlike fülöppite from the Rujevac polymetallic deposit, this one is As-free.

## Sulfosalts of the Cu(Ag)-Fe(Zn)-Sb(As)-S system

Tetrahedrite is a Cu-Sb sulfosalt mineral with following average crystallochemical formula:  $(Cu,Ag)_{10}(Fe,Zn)_{12}Sb_4S_{13}$ . It is the Sb end-member of the continuous solid solution series with As-bearing tennantite. Other elements also substitute in the structure, most notably Fe and Zn, along with less common Ag, Hg and Pb. Bismuth also substitutes Sb, and Bibearing tetrahedrite or annivite is a recognized variety.

Tetrahedrite-group minerals occur in coarse crystalline aggregates only within the Veliki Majdan ore zone. These minerals are closely related to chalcopyrite and bournonite, forming part of the galena-sphalerite mineral assemblage. Furthermore, they usually



Fig. 2. Reflected light and SEM (BSE) photomicrographs of different sulfosalts within the BOF: **a.** Galena overgrown by geocronite and needle-like boulangerite – Kolarica (SEM); **b.** Galena overgrown by bournonite and wooly boulangerite – Centralni revir (SEM); **c.** Needle-like crystals of fülöppite embedded in dolomite matrix – Centralni revir (SEM); **d.** Intergrowth of tetrahedrite with galena which is almost completely replaced by bournonite in pyrite matrix – Kolarica (SEM); **e.** Colloform formations of tennantite-tetrahedrite with zoned pyrite embedded in barite matrix – Bobija (SEM); **f.** Sphalerite overgrown by needle-like zinkenite – Rujevac (reflected light, air, II N); **g.** Ustarasite inclusions in galena embedded in pyrite matrix – Kolarica (SEM); **h.** Elongated and curved lamellae of Ag-bearing nuffieldite embedded in pyrite – Kolarica (SEM); **i.** Intergrowth of bursaite with cannizzarite with needle-like inclusions of tetradymite – Kram (reflected light, oil immersion, II N). Mineral abbreviations: **Gn** – Galena, **Gc** – geocronite, **Bl** – boulangerite, **Br** – bournonite, **Fl** – fülöppite, **Dl** – dolomite, **Th** – tetrahedrite, **Bt** – barite, **Sl** – sphalerite, **Zk** – zinkenite, **Ut** – ustarasite, **Nf** – nuffieldite, **Bs** – bursaite, **Cn** – cannizzarite, **Td** – tetradymite.

cement older cataclastic pyrite aggregates. Tetrahedrite-group minerals rim galena aggregates and are also replaced by boulangerite. According to both, optical observations and measurements in polished sections (microhardness and reflectance spectra) and chemical analyses, two types of tetrahedrite-group minerals can be recognized (RADOSAVLJEVIĆ *et al.* 1986).

EPMA data showed that they belong to the Fe-bearing tetrahedrite –  $(Cu_{9.17}, Ag_{0.60})_{\Sigma 9.77}(Fe_{1.52}, Zn_{0.60}, Cd_{0.02})_{\Sigma 2.14}(Sb_{3.60}, As_{0.27})_{\Sigma 3.87}S_{13.23}$  and Ag-bearing tetrahedrite –  $(Cu_{7.42}, Ag_{2.16})_{\Sigma 9.58}(Zn_{1.13}, Fe_{1.09}, Cd_{0.02})_{\Sigma 2.24}Sb_{4.16}S_{13.02}$  solid solution series. Microhardness of tetrahedrite-group minerals increases with increasing content of Fe and decreasing content of Ag. Tetrahedrite fills cracks and fissures within cataclastic pyrite. Tetrahedrites show variable contents of Zn and Fe (2.2–4.2 and 3.4–5.4 wt%, respectively), whereas some grains contain up to 13.1 wt% Ag. Ag-bearing tetrahedrite is characterized by a Ag/(Ag+Cu) atomic ratio between 0.33 and 0.34. The tetrahedrite-group minerals display Sb/(Sb+As) and Zn/(Zn+Fe) ratios between 0.89 and 1.00 and between 0.27 and 0.31, respectively.

Besides these tetrahedrite-group minerals, new analyses confirmed presence of a Sb-end-member with the lowest Ag content (0.8–1.1 wt%) in the Centralni revir locality (Veliki Majdan ore zone). EPMA analyses yielded following average crystallochemical formula:  $(Cu_{9.85}, Ag_{0.16})_{\Sigma 10.01}(Zn_{1.46}, Fe_{0.53})_{\Sigma 1.99}Sb_{4.01}S_{13.00}$  (4 analyses). It usually crystallizes along galena grain boundaries in a form of elongated crystals, overgrown by bournonite (Fig. 2d). Tetrahedrite shows uniform content of Zn and Fe (5.1–6.0 and 1.5–2.2 wt%, respectively). Zn/(Fe+Zn) atomic ratio amounts between 0.73 and 0.76, which corresponds to the variety with a higher Zn content.

The mineralogical investigation confirmed that the Bobija deposit consists of a simple mineral association composed of sulfides, sulfosalts (tetrahedrite-tennantite group), native Ag, barite and gangue minerals. Tetrahedrites are significantly abundant in the ore. According to the optical features they generally correspond to tennantite, and partly to tetrahedrite. These minerals are often in association with pyrite, sphalerite, and galena but in a lesser extent. Colloform grains of tetrahedrite-tennantite composition are not rare, and are separated from pyrite and sphalerite in the assemblage (Fig. 2e). Occurrence of disperse pyrite in tetrahedrite surfaces when it completely changes its optical features is not rare. Central parts of these aggregates are sometimes seized by zoned pyrite.

EPMA confirmed that tetrahedrite from Bobija is of As-Sb composition with Ag, Hg, and Mn in small amounts (0.7–1.8 wt%, < 0.3–2.2 wt%, and < 0.3–0.5 wt%, respectively). The average EPMA yielded following crystallochemical formula:  $(Cu_{9.82}, Ag_{0.16})_{\Sigma9.98}$  (Zn<sub>1.25</sub>, Fe<sub>0.64</sub>, Hg<sub>0.10</sub>, Mn<sub>0.02</sub>)<sub> $\Sigma2.01$ </sub>(As<sub>2.60</sub>, Sb<sub>1.38</sub>)<sub> $\Sigma3.98$ </sub>

 $S_{13.02}$  (RADOSAVLJEVIĆ *et al.* 2013b). The Sb/(Sb+As) atomic ratio ranges from 0.21 to 0.43 corresponding to a variety with an increased content of tennantite component. These minerals show variable contents of Zn (4.3–6.0 wt%), and Fe (1.7-3.5 wt%). The Zn/(Fe+Zn+Mn+Hg) atomic ratio ranges between 0.5 and 0.7, which corresponds to a variety with an increased Zn content.

#### Sulfosalts of the Ag(Pb)-Bi(Sb)-S system

This group belongs to Ag-rich sulfosalts (pyrargyrite family) and ternary sulfosalts (freieslebenite family) (MoëLo *et al.* 2008). Within the Veliki Majdan ore zone, pyrargyrite was determined only microscopically, embedded in carbonate matrix accompanied with galena (RADOSAVLJEVIĆ 1988).

According to RADOSAVLJEVIĆ *et al.* (2013a), Ag content incorporated in the structure of galena amounts to approximately 15 wt%, while the rest is in a form of micron ("visible") and/or submicron ("invisible") particles of Ag minerals. The following Ag minerals diaphorite, fizélyite, freieslebenite, schirmerite, and Ag-bearing tetrahedrite were determined qualitatively into the insoluble residue using XRD method.

Ore microscopic and EPMA investigations confirmed presence of schirmerite in the Veliki Majdan ore zone (Kolarica locality). It is determined as Sbbearing schirmerite with a following average crystallochemical formula:  $(Ag_{1.96}, Fe_{0.96})_{\Sigma 2.91}Pb_{6.11}(Bi_{5.98}, Sb_{0.84})_{\Sigma 6.82}S_{18.16}$  (5 analyses).

Besides schirmerite, in the same locality a sulfosalt with a following chemical composition was determined (in wt%): S (16.99-17.05), Fe (0.45-2.38), Ag (5.52–6.27), Sb (2.83–6.80), Pb (33.42–36.84), Bi (33.56-36.57). Cu, As and Te are below a detection limit <0.3 wt%. It usually cements cracks and fissures of pyrite crystals and/or is deposited in them, mostly forming a very fine lamina or bent "comb-like" lamellae up to 100 µm in length (Fig. 2h). Luster is moderately high (~35–45 %), microhardness is higher than galena with noticeable pale gray to gray-violet bireflectance. According to optical and chemical characteristics this sulfosalt was defined as Ag-bearing nuffieldite with a following average crystallochemical formula:  $Pb_2(Ag_{0.72}, Fe_{0.30})_{\Sigma 1.02}(Sb_{0.54}, Pb_{0.24}, Bi_{0.21})_{\Sigma 1.00}Bi_{2.00}S_{6.98}$ (4 analyses). According to these analyses Cu has been completely substituted by Ag and Fe (MOËLO et al. 1997; PRŠEK et al. 2006).

#### Sulfosalts of the Pb-Bi-S(Te) system

This group belongs to lillianite homotypic series. The definition and crystal chemistry of this homologous series were presented by MAKOVICKY (1977) and MAKOVICKY & KARUP-MØLLER (1977a, 1977b).

Sulfosalts occurring in the Kram-Mlakva ore zone are related to the pyrite-chalcopyrite mineral assemblage, and are represented by: *bursaite* - ( $Pb_{4,81}$ ,  $Fe_{0.03}$ ,  $(Pb_{1.95}, Cu_{0.08})_{\Sigma 2.03}(Bi_{1.92}, Sb_{0.01})_{\Sigma 1.93}S_{5.05}; aikinite$  - $(Cu_{0.97}, Fe_{0.02})_{\Sigma 0.99}(Pb_{0.98}, Ag_{0.05})_{\Sigma 1.03}Bi_{0.95}S_{3.03};$ croscopically distinguished owing to their very small grain-size. Aggregates were embedded in garnet-calcite matrix. Well-developed crystals have not been observed, only spherical and spindle-like forms up to 10  $\mu$ m in length. In addition, fewer occurrences of these sulfosalts were also determined in the Kolarica locality (Veliki Majdan ore zone), associated with pyrrhotite-sphalerite-galena mineral assemblage (RA-DOSAVLJEVIĆ-MIHAJLOVIĆ et al. 1998, 2007; RADOSA-VLJEVIĆ et al. 2013a).

Bursaite is characterized by complex intergrowths that appear along cracks and fissures of chalcopyrite and silicates in a form of lath-like grains (Fig. 2i). In comparison to the other accompanying Pb-Bi sulfosalts, it is harder. It often contains inclusions of native Bi as exsolution products. According to MOELO *et al.* (2008), bursaite has been discredited as a mineral species. From the Sn-W deposit (Shumilovskoe locality) MOZGOVA et al. (1988) described an almost identical mineral to the one from the Kram-Mlakva ore zone. In their detailed mineralogical work on bursaite and cannizzarite the authors proposed that bursaite should be retained as an intergrowth of two lillianiterelated phases, each with distinct unit-cell parameters. The EPMA composition, which represents a composite of two phases, indicates a Pb deficiency ( $n \approx 3.83$ ). Minerals of bursaite composition from four known localities (Uludag-Turkey, Shumilovskoe-Russia, Cofer-Virginia, and Kram-Mlakva-Serbia) still have a problem of unsolved crystal structure. However, our new evidences, led to confirm that bursaite is undoubtfully a distinct mineral. Unfortunately, numerous attempts to determine the crystal structure using XRD on both single-crystal and powdered samples from the Kram–Mlakva ore zone were not successful, due to a very low crystallinity degree (RADOSAVLJE-VIĆ-MIHAJLOVIĆet al. 2007).

Cannizzarite reflectance is moderately high, but lower than bursaite (Fig. 2i). Reflection pleochroism is distinct, light gray to creamy. The anisotropy is strong, similar to bursaite, and hardness is considerably lowered (similar to galena). According to optical (reflectance, bireflectance, anisotropy) and physical (hardness) characteristics the investigated sulfosalt corresponds to cannizzarite. It is determined on a basis of optical, crystallographic and chemical measurements (RADOSAVLJEVIĆ-MIHAJLOVIĆ *et al.* 2007). Cosalite is less abundant than bursaite and cannizzarite. It occurs along sulfosalt aggregate rims as "jaggy" intergrowth forms. It is white, very similar to galena with trace of cream. Reflection pleochroism is weak and distinct only in oil, light gray to light green. The anisotropy is noticeable, but very distinct in oil with strong illumination. Reflectance and hardness are lower than in bursaite and cannizzarite (RADOSA-VLJEVIĆ 1988).

Aikinite is the least abundant. It occurs in a form of elongated crystals, in a contact with bursaite and chalcopyrite. Hardness is the highest of all sulfosalts of this group. It is white with a light tint of cream. Reflection pleochroism is distinct in air, in oil very striking, light yellow to gray. Anisotropy is also distinct in air, in oil rather high. It is determined on a basis of optical and chemical measurements (RADOSAVLJEVIĆ 1988).

Ustarasite occurs only in the Kolarica locality (Veliki Majdan ore zone) mostly as mutually parallel thin needle-like crystals (up to 100  $\mu$ m in length), and rarely as rhombohedral crystals embedded in older galena and carbonate matrix (Fig. 2g). It is an exsolution product of galena and Bi-Sb-Ag complex compounds. Bireflectance is noticeable, //N strong luster like galena,  $\perp$  N darker with gray tint (quite to that of falkmanite), microhardness similar to cosalite, and anisotropy is strong without internal reflections (RADOSAVLJEVIĆ *et al.* 2013a).

Tetradymite also occurs in sulfosalt aggregates in form of fine needles. It is white, with faint yellowish tinge (Fig. 2i). Bireflection is weak, hardly visible at grain boundaries, light yellow to creamy. The anisotropy is distinct, and reflectance is high ( $R \sim 60 \%$ ). It is determined on a basis of optical and chemical measurements (RADOSAVLJEVIĆ-MIHAJLOVIĆ *et al.* 2007).

## General genetic and paragenetic characteristics

Temperature of deposition of Pb-Zn mineral associations in the BOF range from 480-160 °C (RADOSA-VLJEVIĆ et al. 2012). Galena and sphalerite of this orefield were formed in high-, middle- and low-temperature hydrothermal stage, while Pb-Zn mineral associations of the Pb(Au)-Zn-FeS<sub>2</sub> Veliki Cip and CaF<sub>2</sub>-Pb-Zn Ravnaja deposits unquestionably correspond to the high- (480 °C) and low-temperature hydrothermal stage (230 °C), respectively. In addition, the Pb(Ag)-Zn-FeS<sub>2</sub> Veliki Majdan ore zone corresponds to the temperature range from 450 to 370 °C that is between high- and medium-temperature hydrothermal stages. Temperature decreases moving further from the Tertiary granodiorite of Boranja according to the following sequence: Kolarica-Centralni revir-Kojići. Moreover, in the Ravnaja deposit, NIKOLIĆ & GATTER (1986) determined two temperature intervals of formation of fluorite (275-245 °C and 205-160 °C), and density of fluids (0.98–0.80 g/cm<sup>3</sup>). In addition, temperature range of deposition from 280 to 160 °C was obtained on quartz and sphalerite from the Sb-Pb-Zn-As Rujevac deposit using cryometric method (MUDRINIĆ 1984).

Judging by the look of the exsolution structures of various compositions established in all levels of ore deposits, the temperature of crystallization of all skarn, high-, and middle-temperature hydrothermal associations was identical to formation of isometric coarsecrystalline grain-like structures. However, low-temperature hydrothermal associations characterize finegrained colloform and gel-like textures with regular appearance of recrystallization (RADOSAVLJEVIĆ 1988).

Based on paragenetic relations into the polymetallic deposits of the BOF, the beginning of crystallization is connected to the low partial pressure  $fS_2$ , and deposition of low sulfidization minerals (pyrrhotite, Fe-rich sphalerite, tetrahedrite group of minerals, Pb-Sb and Pb-Bi sulfosalts, etc.). Minerals of high sulfidization (transformation of pyrrhotite into pyrite, pyrite, Fe-poor sphalerite, antimonite, realgar, etc.) began to crystalize with temperature decrease, partial pressure  $fS_2$  increase, and spatial distancing from the Tertiary granodiorite of Boranja. Deposition areas were carbonates (mostly Triassic limestones) and silicates (dacite, andesite, slates), but in a lesser extent (RADOSAVLJEVIĆ *et al.* 2013a).

Silver is important and genetically significant metal which content varies from 10 to 820 g/t in the BOF. Its transport was achieved by polysulfide solutions enriched with Pb, Bi, Sb, and As. However, a possibility of carbonate-bicarbonate and halogen complex solutions should not be excluded. The best correlation is between Ag and Pb (r=0.828 significant at the 95 % confidence level), while among other elements it does not exist. This is expected since galena is the main Ag-bearing mineral, while occurrence of Ag minerals (Ag-tetrahedrite, pyrargyrite, electrum, and native Ag) is limited (RADOSAVLJEVIĆ 1988). Besides Ag, typomorphic elements as Bi and Sb are significantly abundant in galena. Complex investigations of galena from various deposits yielded that it frequently occurs in a form of isostructural solid solutions with diaphorite, fizélyite, freieslebenite, and schirmerite (e.g. WERNICK 1960; ONTOYEV & KORSAKOVA 1967; HODA & CHANG 1975; WANG 1999; CHUTAS et al. 2008).

Crystallization of minerals in the BOF occurred in several successive stages, which together correspond to the unique mineralization cycle. According to the deposited minerals it can be concluded that hydrothermal solutions descend from common magmatic chamber connected to the Tertiary granodiorite of Boranja (RADOSAVLJEVIĆ *et al.* 2013a).

#### Conclusions

The areal extent of the SMMP covers around 30,000 km<sup>2</sup> in the territory of Serbia and extends over

the three major geotectonic units: the Vardar ophiolite zone, the Serbo-Macedonian massif, and the inner Dinarides. It covers a small part of eastern Bosnia and Herzegovina (B&H), larger parts of Serbia and the Former Yugoslav Republic of Macedonia (FYRM), and also extends towards Bulgaria and Greece. The SMMP contains numerous volcanic-intrusive complexes of calcalkaline and shoshonitic affinity. These igneous complexes are directly associated with the development of numerous deposits and metal occurrences; primarily as Pb, Zn, Sb, then Cu and Mn, and to a lesser extent Fe, Bi, Ag, Hg, U, Sn, and W.

Polymetallic deposits of the BOF are genetically connected to the Tertiary granodiorite complex. It consists of a large number of Pb-Zn and Sb sulfide deposits, and in a lesser extent Cu, As, Bi and Ag. Magnetite deposits of lesser importance, connected to Ca-skarn stage, were formed along the contact of Triassic limestones and quartz diorite. Minerals of the BOF are characterized by very diverse types and are consisted of sulfides, sulfosalts, native metals, wolframates, molybdates, oxides, silicates and hydroxides.

The sulfosalts of the BOF can be divided in four main groups: (i) Pb-Sb(As)-S system, with  $\pm$ Fe and  $\pm$ Cu; (ii) Cu(Ag)-Fe(Zn)-Sb(As)-S system; (iii) Ag(Pb)-Bi(Sb)-S system; (iv) Pb-Bi-S(Te) system. These are most abundant in following polymetallic deposits and ore zones: Cu(Bi)-FeS Kram–Mlakva, Pb(Ag)-Zn-FeS<sub>2</sub> Veliki Majdan (Kolarica–Centralni revir–Kojići), Sb-Zn-Pb-As Rujevac, and Pb-Zn-FeS<sub>2</sub>-BaSO<sub>4</sub> Bobija. Among over a hundred ore and rockforming minerals from this area a considerable number of new minerals from the aspects of supplementing systematics of mineralogy of Serbia have been discovered.

Pb-Sb sulfosalt mineral assemblages are widespread throughout SMMP, where following orefields and ore zones are distinguished by its diversity: Kopaonik (Rajićeva Gora, Belo Brdo, Rogozna, etc.), Kratovo-Zletovo, Toranica, Sasa, Bučim, Alšar, etc. (e.g. JANKOVIĆ & ZARIĆ 1980; JANKOVIĆ 1993; SER-AFIMOVSKI & ALEKSANDROV 1995; ALEKSANDROV et al. 1990A; Aleksandrov et al. 1990B; Serafimovski et al. 1990; SERAFIMOVSKI et al. 2006; SERAFIMOVSKI et al. 2013; SERAFIMOVSKI et al. 2015; RADOSAVLJEVIĆ & DIMITRIJEVIĆ 2001; VOUDOURIS et al. 2008; RADO-SAVLJEVIĆ & STOJANOVIĆ 2013; RADOSAVLJEVIĆ et al. 2014B). Besides the BOF, similar Pb-Bi(Sb) sulfosalt mineral assemblages have been determined in the Central Serbia, the Šumadija Metallogenic District, Rudnik orefield (STOJANOVIĆ et al. 2006) and Golija orefield (STAJEVIĆ & ZARIĆ 1984). According to the mineral compositions, they are close to the Uludag orefield, Bursa Province, Turkey (VAN DER KAADEN 1958; MAKOVICKY & KARUP-MØLLER 1977), the Stanos shear-zone related deposit, Chalkidiki, Northern Greece (VOUDOURIS et al. 2013), and in the Trepča deposit, Stari Trg, Kosovo, Serbia (KOŁODZIEJCZYK et al. 2015), belonging to the Alpine metallogenic belt. Also, these mineral assemblages are very similar to the Larga hydrothermal systems in Romania (Carpathian-Balkan metallogenic province - COOK & CIOBA-NU 2004). Moreover, in comparison to the other metallogenic district within the SMMP, the mineral associations of the BOF are distinguished by a variety of Ag(Pb)-Bi(Sb) sulfosalts.

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#### Резиме

#### Преглед сулфосолне групе минерала у Pb-Sb(As)-S, Cu(Ag)-Fe(Zn)-Sb(As)-S, Ag(Pb)-Bi(Sb)-S и Pb-Bi-S(Te) системима са рудног поља Борање, Западна Србија

У Српско-македонској металогенетској провинцији (СММП), која просторно захвата мањи део Источне Босне, веће делове Србије и Македоније, и наставља даље према Бугарској и Грчкој, јављају се бројне и простране масе вулкано-плутонских комплекса калко-алкалне магме. Површина њиховог развића у Србији износи око 30.000 km<sup>2</sup> и простире се преко три крупне геотектонске јединице: Унутрашњи Динариди, Вардарска тектонска зона и Српско-македонска маса. У вези са овим магматским комплексима, директним или индиректним, дошло је до стварања бројних лежишта и појава метала, у првом реду Рb, Zn, Sb, затим Сu, Mn, у мањој мери Fe, Bi, Ag, Hg, U, Sn и W.

Подрињска металогенетска област припада СММП. Мање металогенетске јединице су издвојене у оквиру следећих рудних поља: Цер (Северна Србија), Борања (Западна Србија) и Сребреница (Источна Босна). Полиметалична лежишта у рудном пољу Борање генетски су везана за терцијарни гранодиоритски комплекс. Састоје се од великог броја сулфидних лежишта са Pb-Zn, и Sb; и у мањој мери са Си, As, Bi и Ag. Међу њима, јављају се мања значајна лежишта магнетита, која су у вези са скарновском етапом. Скарнови су калцијског типа, а формирани су дуж контаката тријаских кречњака и кварц диорита. У рудном пољу Борање, рудни и нерудни минерали одликују се веома разноврсним врстама и састоје се од сулфида, сулфосоли, самородних метала, волфрамата, молибдата, оксида, силиката и хидроксида.

Минерале из групе сулфосоли, који се јављају у лежиштима и појавама рудног поља Борање, могу се поделити у четири веће групе, са следећим до сада одређеним минералима: (i) систем Pb-Sb(As)-S, са  $\pm$ Fe и  $\pm$ Cu – цинкенит, филопит, плагионит, робинсонит, буланжерит, џемсонит, бурнонит, Asбурнонит, твинит, геокронит и гратонит; (ii) систем Cu(Ag)-Fe(Zn)-Sb(As)-S – тетредрит, тенантит, и Ag-тетредрит; (iii) систем Ag(Pb)-Bi(Sb)-S – пираргирит, дифорит, фрајслебенит, Sb-ширмерит, Ag-њуфилдит и физелит; (iv) систем Pb-Bi-S(Te) - бурсаит, каницарит, козалит, ајкинит, устарасит и тетрадимит.

Ове сулфосоли су просторно широко распрострањене у оквиру рудног поља Борање, међутим, оне су најзаступљеније у следећим полиметаличним лежиштима и рудним зонама: Cu(Bi)-FeS Крам-Млаква; Pb(Ag)-Zn-FeS<sub>2</sub> Велики Мајдан (Коларица–Централни ревир–Којићи); Sb-Zn-Pb-As Рујевац; Pb-Zn-FeS<sub>2</sub>-BaSO<sub>4</sub> Бобија. Осим ових, до сада откривених сулфосоли, са сигурношћу постоји вероватноћа откривања и нових минерала из ове групе, а нарочито треба очекивати код познатог сулфосолног система Pb-Ag-Bi-Sb-S. Од преко стотинак одређених рудних и нерудних минерала на овом подручју, откривен је и знатан број нових минерала са аспеката допуњавања систематике минералогије Србије, и шире. У овој студији изложена је синтеза досадашњих резултата истраживања на минералима из групе сулфосоли, која су већим делом публикована од стране аутора, међутим, овде су дати допуњени, а такође, и нови подаци.

Рb-Sb сулфосолне минералне парагенезе најзаступљеније су у скоро целој СММП, где се по својој разноликости ових минерала издвајају: рудно поље Сребренице, Копаоничка рудна зона (Рајићева Гора, Бело Брдо, Црнац, и др.), рудна поља Кратово-Злетово, Тораница, Саса, Бучим и Алшар (Македонија), и друга. Поред рудног поља Борање, сличне Pb-Bi сулфосолне минералне парагенезе утврђени су у рудним пољима Рудника (Шумадија) и Голије (Копаоник).

Поред рудног поља Борање, сличне Pb-Bi(Sb) сулфосолне минералне парагенезе утврђене су у рудним пољима Рудника и Голије. Према минералном саставу, она су у веома сличне рудном пољу Улудаг (Бурса, Турска), минерализацијама на Станос (Халкидики, Северна Грчка) и рудном пољу Трепча (Стари Трг, Косово, Србија), која су такође део алпске металогенетске јединице. Такође, ове Pb(Ag)-Ві сулфосолне минералне парагенезе веома су сличне хидротермалним системима Ларга у Румунији (Карпато-балканска металогенетска провинција). На крају, у поређењу са осталим областима у СММП, минералне асоцијације рудног поља Борања одликује се са јединственим минералима и варијететима из посебне групе Ag(Pb)-Bi(Sb) сулфосоли.

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#### Chert blocks in the ophiolitic mélange of Zlatibor Mt. (SW Serbia) – age and geodynamic implications

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Abstract. Cherts are quite frequently occurring rocks in the Internal Dinarides, an extremely complex area composed of several tectonostratigraphic units in which oceanic sediments, ophiolites and partly metamorphosed parts of the distal continental margin of Adria are preserved. Therefore, these cherts differ in age and the original depositional environment in which they were formed.

Results of investigations carried out in the chert blocks found in the mélange in the vicinity of Jasenovo village on SE slopes of Zlatibor Mt. are presented here. Radiolarian cherts from the studied localities represent blocks in mélange of the East-Bosnian–Durmitor Unit, exposed in a large tectonic window below the Triassic carbonates of Drina–Ivanjica Unit. Biostratigraphic data revealed Callovian–early Kimmeridgian ages of the studied chert blocks, thus implying a Kimmeridgian or younger age of obduction of the West Vardar ophiolites.

Key words: Cherts, radiolarians, ophiolitic mélange, Jurassic, Internal Dinarides, SW Serbia.

Апстракт. Рожнаци се често срећу у Унутрашњим Динаридима, изузетно комлексној области изграђеној од неколико тектоностратиграфских јединица у којима су сачувани океански седименти, офиолити и делимично метаморфисани делови дисталне маргине Адрије. Тако се на овом простору појављују рожнаци различите старости формирани у различитим депозиционим срединама.

У овом раду приказани су резултати истраживања рожначких блокова у меланжу у близини села Јасеново на ЈИ падинама Златибора. Радиоларијски рожнаци са истраживаних локалитета представљају блокове у меланжу Источнобосанско-дурмиторске јединице, откривеном у тектонском прозору испод тријаских карбоната Дринско-ивањичке јединице. Биостратиграфском анализом добијена је келовејско-доњокимериџска старост истраживаних блокова рожнаца, што указује да је обдукција Западно-вардарских офиолита била током кимериџа или касније.

Кључне речи: Рожнаци, радиоларије, офиолитски меланж, јура, Унутрашњи Динариди, ЈЗ Србија.

#### Introduction

Precise dating of wide variety of oceanic sediments is necessary for reconstructions of palaeogeography and geodynamic evolution of oceanic basins and their continental margins. In that sense, radiolarian biostratigraphy is extensively used today in dating pelagic marine sediments. Investigations of radiolarian associations carried out so-far in the Internal Dinarides of Serbia reveal the following age clusters: Middle to Late Triassic, Middle Jurassic and Late Cretaceous. Early Jurassic ages have not been proven in the Internal Dinarides in Serbia, while Upper Jurassic ages have been questioned recently.

Both Triassic and Jurassic radiolarians occur in chert blocks embedded in mélange of Late Jurassic age in the Internal Dinarides (e.g. OBRADOVIĆ *et al.* 1987/88; GORIČAN *et al.* 1999; VISHNEVSKAYA *et al.* 2009; OZSVÁRT & KOVÁCS 2012; GAWLICK *et al.* 2009; DJERIĆ *et al.* 2010).

Triassic ages are obtained for oceanic sediments associated with MORB-like and within-plate basalts

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(OBRADOVIĆ *et al.* 1987/88; VISHNEVSKAYA *et al.* 2009), while Middle Jurassic ages are established for pelagic sediments that stratigraphically overlie platform carbonates of the passive margin of Adria (e.g. DJERIĆ *et al.* 2007, 2012), as well as from ophiolitebearing detrital sediments formed during the obduction of the ophiolites onto the adjacent continental margin (OBRADOVIĆ & GORIČAN 1988; VISHNEVSKAYA *et al.* 2009; DJERIĆ *et al.* 2010). Late Cretaceous radiolarians are found in sedimentary cover of ophiolitic mélange of the Western Vardar Zone (e.g. DJERIĆ *et al.* 2009; BRAGINA *et al.* 2014; DJERIĆ & GERZINA 2014).

The aim of this paper is to present results of investigations carried out in the chert blocks found in the mélange in the vicinity of Jasenovo village on SE flanks of Zlatibor Mt.

#### **Geological setting**

The study area is situated in SW Serbia. In a geotectonic sense, it is a part of the Internal Dinarides, DIMITRIJEVIĆ, M.D. 2001; DIMITRIJEVIĆ *et al.* 2001, 2003; KARAMATA 2006).

According to other opinions (e.g. BERNOULLI & LAUBSCHER 1972; BAUMGARTNER 1985; PAMIĆ 1998; PAMIĆ et al. 2002; CSONTOS et al. 2003, 2004; BORTO-LOTTI et al. 2004, 2013; BORTOLOTTI & PRINCIPI 2005; SCHMID et al. 2008) all these ophiolites derived from a single ocean and were thrusted onto the continental margin of Adria. According to these interpretations, continental (Drina-Ivanjica, Jadar, and East-Bosnian-Durmitor) blocks which separate two ophiolite belts are tectonic windows below the obducted ophiolites, in which the most distal parts of Adria are exposed (Fig. 1). This implies that ophiolites formed single, continuous sheet referred to as the Western Vardar Ophiolitic Unit that was obducted during the Late Jurassic (CSONTOS et al. 2003, 2004; SCHMID et al. 2008) and includes all ophiolites of the Dinarides west of the Sava Zone. Subsequent out-of-sequence thrusting resulted in formation of composite units made up of the continental margin of Adria, ophiolitic mélange and obducted ophiolites.



Fig. 1. Tectonic sketch of the Dinarides (modified after SCHMID *et al.* 2008; SCHEFER *et al.* 2010), with indicated position of the studied localities.

geologically extremely complex area composed of several tectonostratigraphic units in which oceanic sediments, ophiolites and partly metamorphosed parts of the distal continental margin of Adria are preserved.

Dinaridic ophiolites have been considered as remnants of two different oceanic basins by majority of Serbian authors working in the Dinarides (e.g., MAK-SIMOVIĆ 1975; DIMITRIJEVIĆ & DIMITRIJEVIĆ 1973, 1974, 1975, 1976, 1979; PAMIĆ & MAJER 1977; KARA-MATA *et al.* 1980; PAMIĆ 1983; LUGOVIĆ 1986; RO-BERTSON & KARAMATA 1994; KARAMATA *et al.* 1999;

#### **Methods**

Two samples were collected from chert blocks found in the mélange in the vicinity of Jasenovo village on SE flanks of Zlatibor Mt. All the productive samples are radiolarian cherts and were treated with diluted 7% hydrofluoric acid, following the method of PESSAGNO & NEWPORT (1972). The radiolarians are generally poorly preserved. The assemblages were dated with the zonation of BAUMGARTNER *et al.* (1995). The data obtained during the last 15 years show that some

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species have longer ranges than previously established by BAUMGARTNER *et al.* (1995). The age assignments are discussed below. Generic names have been updated according to O'DOGHERTY *et al.* (2009).

The SEM microscope ISI-160 in GIN RAN (Moscow) (sample NĐ 132) and JEOL JSM - 6460LV SEM at the Department for Biology and Ecology, University of Novi Sad (sample NĐ 108) were utilized for the precise identification and illustration of the radiolarians. All the material examined is deposited at the Faculty of Mining and Geology, University of Belgrade.

#### Description of outcrops and biostratigraphy

The studied samples were collected from two chert outcrops on SE slopes of Zlatibor Mt. (Fig. 2).

The locality Rauke is situated 3 km east of village Jasenovo (x = 7412597, y = 4824315). It is about 1.5 m thick succession of greenish, dark gray and black stratified chert with thin interlayers of siliceous shale (Fig. 3). Average thickness of chert layers is 3–6 cm, but it exceeds 15 cm in places.

Sample NĐ 132, taken at this locality, is characterized by a relatively poorly preserved radiolarian association. Presence of species *Praewilliriedellum robusta* (MATSUOKA) indicates a latest Bajocian to early Callovian age of the sediment (UAZs 5-7). The association can not be younger than the Callovian, which is confirmed by the presence of species *Belleza decora* (RUST) whose last occurrence is in UAZ 7, (BAUM-GARTNER *et al.* 1995). Besides these characteristic species, the radiolarian association in the sample NĐ 132 comprises also *Transhsuum maxwelli* gr. (PES-SAGNO), *Transhsuum* sp. aff. *T. maxwelli, Transhsuum* 



Fig. 2. Simplified geologic map of the wider investigation area (modified after DJERIĆ et al. 2012).



Fig. 3. Chert block at the locality Rauke.

*brevicostatum* gr. (OZVOLDOVA), *Tethysetta baloghi* (KOZUR), *Transhsuum* sp., *Napora* sp., *Stichomitra* sp. and *Praewilliriedellum* sp. (Fig. 4).

Transhsuum sp. cf. T. maxwelli gr., Eucyrtidiellum ptyctum (RIEDEL & SAN FILIPPO), Zhamoidellum ventricosum DUMITRICA, Zhamoidellum ovum DUMITRI-CA, Zhamoidellum sp. cf. Z. ovum, Zhamoidellum sp. cf. Z. kozuri (HULL), Williriedellum frequens (TAN SIN HOK) and Cryptamphorella sp. (Fig. 6).

According to BAUMGARTNER et al. (1995), the last occurrence of Transhsuum maxwelli gr. is reported in UAZ 10. Acording to the same authors, Zhamoidellum ventricosum is known from the UAZ 8-11, but it has recently been reported also from assemblages of UAZ 6-7 (e.g. ŠMUC & GORIČAN 2005; O'DOGHERTY et al. 2006; CHIARI et al. 2013) and is no more considered to have its first occurrence in UAZ 8. Zhamoidellum ovum is, according to BAUMGARTNER et al. (1995) known from the interval Middle-Late Oxfordian to Late Kimmeridgian-Early Tithonian (UAZ 9-11). However, according to SUZUKI & GAWLICK (2003), this species has its first occurrence in Callovian. Also Cinguloturris carpatica has its first occurrence in UAZ 7 (BAUM-GARTNER et al. 1995). Originally, this zone comprised the late Bathonian and early Callovian (BAUMGARTNER



Fig. 4.. Middle Jurassic radiolarians from the Rauke locality. **1**, **2**, *Praewilliriedellum* sp. cf. *P. robusta* (MATSUOKA), ×300; **3**, **4**. *Praewilliriedellum* sp., ×200; **5**. *Belleza decora* (RUST), ×300; **6**. *Stichomitra* sp., ×200; **7**. *Tethysetta baloghi* (KOZUR), ×200; **8**, **9**. *Transhsuum maxwelli* gr. (PESSAGNO), ×200; **10**. *Transhsuum* sp. aff. *T. maxwelli* (PESSAGNO), ×200; **11**. *Transhsuum* sp., ×200; 12. *Transhsuum brevicostatum* gr. (OZVOLDOVA), ×200; **13**. *Napora* sp., ×200

At the locality Marića Potok, in a creek near village Jasenovo (x = 7411278, y = 4822274), there is an outcrop of 8 m thick red thin-layered chert with thin interlayers of siliceous shale (Fig. 5).

Sample NĐ 108, taken at this locality, contains the following radiolarian association: *Cinguloturris carpatica* DUMITRICA, *Transhsuum maxwelli* gr. (PESSAGNO),

*et al.* 1995). A diverse radiolarian assemblage of UAZ 7 was subsequently described from a sample above the early Callovian ammonites, which led to the conclusion that UAZ 7 is mainly Callovian in age (BECCARO 2006).

According to these data, this sample is not older than the Callovian and not younger than late Oxfordian–early Kimmeridgian.



Fig. 5. Chert block at the locality Marića Potok (Photo courtesy of Milan Sudar and Divna Jovanović).

been proven yet in the territory of Serbia. Radiolarian cherts of Jurassic age, which represent the uppermost part of the obducted oceanic crust, appear to be preserved in Albania only (e.g. CHIARI *et al.* 1994; PRELA *et al.* 2000).

Jurassic-age radiolarian cherts are also found as an integral part of the "*in situ*" preserved passive margin sedimentary sequence in the footwall of the ophiolitic mélange (East-Bosnian–Durmitor and Drina–Ivanjica units) (DJERIĆ *et al.* 2007, DJERIĆ *et al.* 2012, RADO-IČIĆ *et al.* 2009). Such radiolarites were originally deposited onto Triassic and Lower Jurassic carbonaceous platform sedimentary sequence of the passive margin were subsequently torn-off and incorporated in the mélange at the front of the obducting nappe.

Although there are outcrops of basalt pillow-lavas in the immediate vicinity of the studied localities, no



Fig. 6. Middle to Late Jurassic radiolarians from the Marića potok locality. Scale bar 50 μm (2–11); 100 μm (1). **1.** *Transhsuum maxwelli* gr. (PESSAGNO); **2, 3.** *Transhsuum* sp. cf. *T. maxwelli* gr. (PESSAGNO); **4.** *Cinguloturris carpathica* DUMITRICA; **5.** *Williriedellum frequens* (TAN SIN HOK); **6, 7.** *Zhamoidellum ovum* DUMITRICA; **8.** *Zhamoidellum* sp. cf. *Z. ko zuri* (HULL); **9.** *Zhamoidellum ventricosum* DUMITRICA; **10.** *Cryptamphorella* sp.; **11.** *Eucyrtidiellum ptyctum* (RIEDEL & SANFILIPPO)

#### **Discussion and conclusions**

Middle Jurassic radiolarian cherts are abundant in the region. A widely accepted opinion among Serbian geologists (e.g. RADOVANOVIĆ 1987; KARAMATA 2006) is that these rocks represent a sedimentary cover of the Neotethyan oceanic crust. However, a clear association of Jurassic cherts with MOR basalts has not stratigraphic contact with cherts has been observed. This confirms previous observations that there are no radiolarites associated with mid-ocean-ridge related basalts which would represent the uppermost part of the Jurassic oceanic crust in the Dinarides. Therefore, the studied cherts probably did not derive from the sedimentary cover of the ocean floor, but from the distal parts of the passive margin of Adria. Besides, field



Fig. 7. Geological cross-section through the SE flanks of Zlatibor Mt. with indicated positions of the studied localities.

observations show that all these rocks are in a large tectonic window below the Triassic carbonates of Drina–Ivanjica Unit. Accordingly, radiolarian cherts from the studied localities at the SE flanks of Zlatibor Mt. represent blocks in mélange of the East-Bosnian–Durmitor Unit (Figs. 2, 7).

The age of mélange formation, and hence of the final stages of obduction of the West Vardar ophiolites is equal to, or younger, than the youngest dated blocks in the mélange. Radiolarian age obtained for the chert block at the locality Rauke is rather similar to that of the previously dated radiolarite blocks in the Serbian Dinarides (GAWLICK et al. 2009; VISHNEVSKAYA et al. 2009; DJERIĆ et al. 2010). The radiolarian association identified from the chert sample from the locality Marića Potok certainly represents the youngest so-far determined age (Callovian - early Kimmeridgian) of chert blocks in the mélanges in this part of the Dinarides. This implies a Kimmeridgian or younger age of obduction of the West Vardar ophiolites. This age, however, should be taken with extreme caution because such a wide age interval could be a result of low diversity and poor-to-moderate level of preservation of the analyzed radiolarian association. Nevertheless, the obtained data perfectly comply with timing of obduction of the Jurassic Neotethyan oceanic crust based on radiometric ages (179-150 Ma) obtained from metamorphic soles in the Dinarides and Hellenides (e.g. SPRAY et al. 1984).

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#### Резиме

#### Блокови рожнаца у офиолитском меланжу Златибора (ЈЗ Србија) – старост и геодинамичке импликације

Прецизно одређивање старости различитих океанских седимената је неопходно за реконструкције палеогеографских прилика и геодинамичке еволуције океанских басена и њихових континенталних маргина. У том смислу се биостратиграфска анализа радиоларијских асоцијација данас често користи за одређивање старости пелашких маринских седимената.

Досадашња истраживања радиоларијских асоцијација у Унутрашњим Динаридима показују да се у меланжу ЈЗ Србије налазе блокови рожнаца тријаске и јурске старости. Тријаски рожнаци углавном представљају делове океанске коре Неотетиса, док јурски представљају стратиграфску повлату платформних кречњака таложених на пасивној маргини Адрије (нпр. DJERIĆ *et al.* 2007, 2012) или блокове у офиолитском меланжу формираном током обдукције офиолита на оближњу континенталну маргину (OBRADOVIĆ & GORIČAN 1988; VISHNEVSKAYA *et al.* 2009; DJERIĆ *et al.* 2010).

Биостратиграфски подаци добијени из блокова у меланжу су значајни јер је старост меланжа, а тиме и време финалних стадијума обдукције западно-вардарских офиолита дефинисана старошћу најмлађих блокова у меланжу. У овом раду презентовани су резултати истраживања блокова рожнаца на два локалитета у близини села Јасеново на ЈИ падинама Златибора.

Старост блока рожнаца на локалитету Рауке (келовеј) одговара претходно добијеним старостима блокова јурских радиоларита у српском делу Динарида (Gawlick *et al.* 2009; Vishnevskaya *et al.* 2009; Djerić *et al.* 2010). Радиоларијска асоцијација из блока рожнаца на локалитету Марића поток, међутим, представља најмлађу до сада одређену старост (келовеј – доњи кимериџ) рожначких блокова у меланжу у овом делу Динарида.

Ово упућује на кимериџску или пост-кимериџску обдукцију западно-вардарских офиолита. Ову старост, међутим, треба узети са извесном резервом, јер овако широк временски интервал може бити добијен услед слабог диверзитета и лошије очуваности радиоларијске асоцијације. У сваком случају, добијени подаци одговарају времену обдукције неотетиских офиолита добијеном радиометријским методама (179–150 Ма) из метаморфних ђонова у Динаридима и Хеленидима (нпр. SPRAY *et al.* 1984).

Средњојурски рожнаци се често срећу на простору Унутрашњих Динарида. Широко распрострањено мишљење међу српским геолозима је да ове стене представљају седиментни покров океанске коре Неотетиса. Међутим, јасна асоцијација јурских рожнаца са базалтима средњоокеанских гребена није пронађена на простору Србије. Јурски радиоларити се такође појављују као део "in situ" сачуваних седимената пасивне маргине у подини офиолитског меланжа (Источнобосанскодурмиторска и Дринско-ивањичка јединица). Радиоларити су таложени преко тријаских и доњојурских седимената карбонатне платформе да дисталној маргини Адрије. Део ових седимената је откинут са пасивне маргине и инкорпориран у меланж на фронту обдукционе навлаке.

Иако постоје изданци базалтних пилоу лава у непосредној близини истраживаних изданака, нормалан стратиграфски контакт са рожнацима није запажен. Ово је у складу са претходним закључцима о непостојању асоцијације јурских радиоларита са базалтима средњоокеанског гребена, односно горњих делова јурске океанске коре у Динаридима, те истраживани блокови рожнаца вероватно потичу са дисталних делова пасивне маргине Адрије. Осим тога, теренска истраживања показују да се ове стене налазе у великом тектонском прозору испод тријаских карбоната Дринско-ивањичке јединице. Имајући све наведено у виду, радиоларијски рожнаци истраживаних локалитета на СИ падинама Златибора представљају блокове у меланжу Источнобосанско-дурмиторске јединице.

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#### Hydrogeologic structures in two Serbian spa towns – Sijarinska banja and Selters banja

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Abstract. The objective of the paper is to identify the boundaries of hydrogeologic structures in which natural mineral waters occur, using two examples: old mineral water (Sijarinska Banja) and young mineral water (Selters Banja). The research addresses the distance from recharge zones, depth of occurrence, and points of discharge. Apart from the three spatial dimensions, the study also includes the time dimension – water age. The following parameters are examined: geologichydrogeologic conditions in the places of occurrence of mineral water, connection between mineral water and permeable fault zones, distance of surface water divides, previously-defined maximum possible depths of occurrence, possible flow rates, and the determined age. If the flow followed a straight line, the maximum distance of the recharge zone would be up to 7 m for the young and up to 11 km for the old mineral water. However, it is obvious that this is never the case in fractured systems, given that water travels much longer distances from the point of entry to the point of drainage from aquifers. Assessment of geologic-hydrogeologic and hydrodynamic conditions, relative to the determined age of the mineral water, leads to the conclusion that the distance between the recharge and drainage zones can be less than 5 km. The paper shows that insight into the depth of infiltration into permeable fault zones can also be gained by studying the depth of circulation relative to known hydrodynamic zones. The inference is that the largest amount of groundwater is restored in the hydrodynamic zone of slow groundwater renewal, which is below a depth of 1.5 km at Sijarinska Banja and below 1.3 km at Selters Banja.

Key words: spread, fault zone, distance of recharge zone, depth, hydrodynamic zoning, mineral water.

Апстракт. Циљ овог рада био је да се на примеру једне од старијих (Сијеринска б.) и једне од млађих ("Селтерс" б.) угљокиселих минералних вода Србије дефинишу границе пространства хидрогеолошких структура у којима се оне формирају. Истраживане су у свом пространству постојања, између области прихрањивања, дубине залегања и зона истицања угљокиселих вода. Осим трију просторних у разматрање је укључена и димензија време – старост вода. За ова истраживања су узети у обзир: геолошко – хидрогеолошки услови области формирања угљокиселих вода, неоспорна веза угљокиселих вода и водопропусних разломних зона, удаљеност површинских вододелница, раније дефинисана теоретска максимална могућа дубина залегања ових структура, могућа брзина кретања вода у датим хидродинамичким условима и утврђена њихова старост. Показало се, да би у случају праволинијског кретања вода, максимална удаљеност области прихрањивања износила, за млађе воде до 7 km, а за старије до 11 km. Међутим, било је јасно да у пукотинским системима то никада није случај, будући да воде прелазе далеко дуже путање у односу на праволинијско растојање од места уласка до места истицања из датих водоносних средина. Из анализе геолошко – хидрогеолошких и хидродинамичких услова, а за утврђене старости вода, закључено је да удаљености између области прихрањивања и зона дренирања могу да буду и мање од 5 km. У раду је показано да се дубина досезања инфилтрационих вода у водопропусним разломним зонама може сагледати и анализом дубина њихове циркулације у односу на познате хидродинамичке зоне. Закључено је да се главна количинска измена одвија у домену хидродинамичке зоне успорених процеса водозамене, која код Сијаринске бање досеже испод 1,5 km, а испод 1,3 km дубине код "Селтерс" бање.

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**Кључне речи:** пространство, разломна зона, удаљеност области прихрањивања, дубина залегања, хидродинамичка зоналност, минерална вода.

#### Introduction

In Serbia, there are more than 65 naturally-carbonated thermal mineral water sites. Many authors have provided brief geological and hydrogeological descriptions of the immediate spread of the hydrogeologic structures in which such water occurs, and presented results of physicochemical, radioactivity and isotope testing (ČEKIć 2013; MILANOVIĆ *et al.* 2012; PROTIĆ 1995; MILOJEVIĆ 1964, 1954). Given the large number of occurrences in Serbia, this research addresses only two: the spa towns of Sijarinska Banja (old mineral water) and Selters Banja (young mineral water).

It is without doubt that the origin of the mineral waters is associated with permeable tectonic structures (LONBARDI & VOLTATTORNI 2010; WEIMLICH 2005, WEIMLICH *et al.* 2003, 1998; CERON *et al.* 2000; GREBER 1994). On the one hand, they allow carbon dioxide from the depth of origin to migrate toward the ground surface and, on the other hand, meteoric water to be infiltrated into deep formations.

The main hydrogeologic structures of Sijarinska Banja and Selters Banja are active and disjunctive fault zones. In the case of the former, it is a large interbloch structure in a low mountainous area, and in the latter an inter-bloch structure in a zone of horsts and trenches, covered by thick Tertiary strata (MARINKO-VIĆ, 2014). At Sijarinska Banja, the mineral water has always been free-flowing, whereas at Selters Banja it was detected inadvertently, given that there were no manifestations on the ground surface.

The hydrogeologic structures were studied in terms of their spread between recharge zones, depth, and points of discharge of mineral water, along with the post-infiltration residence time. The research was based on the indisputable relationships between the mineral water and the regional permeable fault zones, the identified maximum possible depth of the hydrogeologic structures (MARINKOVIĆ et al. 2013), the potential (theoretical) average mineral water flow velocity in the given setting, and the determined age of the mineral water. The distances from surface water divides, along the permeable regional faults in which the mineral water occurs, were also taken into account. These distances were additionally used to estimate the average velocity of groundwater flow. In view of the above, as well as the fact that in fractured aquifers groundwater travels a much longer distance than it would along a straight line from the point of infiltration to the point of drainage (descending and ascending pathways, meandering in 3D space), it was concluded that the consideration of the hydrogeological structure, this distance may be less than 5 km.

The depths of the hydrogeologic structures at Selters Banja and Sijarinska Banja were considered relative to known hydrodynamic zones (high, low and very low rates of groundwater renewal). The results show that the largest amount of water is restored in the hydrodynamic zone of slow groundwater renewal.

It follows from the results of this research that the identified linear directions (tectonic zones) and approximated ultimate boundaries of the hydrogeologic structures are quite reliable and that this knowledge will facilitate exploration aimed at increasing the capacity of water sources, detecting thermal groundwater or addressing other specific tasks.

#### Method

For consideration of the issue of this work were used available to us the results of previous research. They relate primarily to the age of mineral water, rate of groundwater flow in the analog lithological environments and hydrodynamic conditions and the results achieved hydrogeological research in narrow fields of mineral water.

Given that exploration has shown that the fractured hard rocks (schists, igneous rocks, limestones, marls) comprise the main setting of the fault zones in which the mineral water occurs, the average velocity through the hydrogeologic structures was assumed based on the theoretical velocity of groundwater flow in fractured schists (from  $n \times 10^{-8}$  to  $n \times 10^{-4}$  m/s), and the theoretical velocity in the hydrodynamic zone of slow groundwater renewal, which is greater than 0.2 m/year or 6.3×10<sup>-9</sup> m/s (DRAGIŠIĆ 1997). Recognizing these theoretical velocities, it was assumed that the relation between the travel distance and velocity must be such that the recharge zones are in the catchment area in which the mineral water occurs. The average flow velocity was first estimated for Selters Banja, where the geologichydrogeologic conditions are such that it is obvious that the recharge zone is within the catchment of the Alinac River (MILOJEVIĆ 1964). Given that the determined age of the mineral water at Selters Banja is 19,300 years, the average flow velocity must be about  $1.15 \cdot 10^{-8}$  m/s (within limits of the theoretical range). As such, if a higher than average flow velocity was assumed, the distance would have been unrealistically large or the meandering of the flow in 3D space so extensive as to increase the travel distance multiple times relative to the linear distance. For this reason, and taking into account the threshold values of groundwater flow velocities in schists, the lower (slower) limit was assumed for the average flow velocity  $-1.1 \cdot 10^{-8}$  m/s. This average flow velocity is also consistent with the theoretical velocities within the hydrodynamic zone of slow groundwater renewal.

The depth of the mineral water in the hydrogeologic structures was defined relative to the depths of known hydrodynamic zones: rapid, slow and very slow groundwater renewal.

#### **Results and discussion**

#### Geologic-hydrogeologic setting

The mineral water at Selters Banja in the City of Mladenovac occurs near the confluence of the Lug River and its right-bank tributary the Alinac (Fig. 1). It is withdrawn from wells near the right banks of the two rivers. This mineral water was discovered inadvertently in 1898, while Atanasijević brothers were drilling a 239 m deep well on their farm (PROTIĆ



Fig. 1. Geological-hydrogeological map of the area of occurrence of mineral water at Selters Banja: **1.** complex of Neogene sediments; **2.** Mesozoic bedrock (carbonate rocks, flysch and serpentinites separated by faults); **3.** fault structure (a. Lužni-ca–Topčider fault; b. Varovnica fault; c. Alinac River Fault); **4.** recharge zone; and **5.** drainage zone.

1995). The rate of free flow was 1.3 l/s and the water temperature 31.5 °C. It was believed that this well tapped an aquifer in Sarmatian sediments and that recharge occurred in the upper part of the Alinac River catchment, where hard bedrock is exposed (MILOJEVIĆ 1964). Two wells at Selters Banja that tap Lower Cretaceous carbonate rocks have been drilled up to a depth of 816.4 m (MILOJEVIĆ & TOMIĆ 1978) and 1150 m (POLIĆ 1983), respectively. The rocks are slightly karstified and deemed to form the main aquifers at depths below 800 m. This depth was reached by drilling through Neogene sediments, whose thickness at Selters Banja is estimated at 238–275 m. Upper Cretaceous sediments (flysch) were detected between these strata and a main aquifer, which are widely exposed in the west, in the upper catchment of the Alinac River. They are generally represented by marls and sandstones. An 816.4 m deep well partly tapped mineral water from this flysch sequence, in the depth interval 613–816 m. The groundwater temperature was 48–50 °C and its composition similar to that of the previously extracted groundwater. The groundwater was saline (TDS 7.3 g/l) and the pH level was 6.9. The concentration of carbon dioxide was 0.34 g/l and that of radium 0.52 Bq/l.

Recent exploration has corroborated reserves of 6 l/s of mineral water of the ClHCO<sub>3</sub> – Na type, with a TDS level of 6.76 g/l and CO<sub>2</sub> concentrations from 443 to 567 mg/l (ČEKIĆ 2013). The conclusion was that recharge occurs through infiltration of meteoric water along the edges of the basin, where Lower Cretaceous sediments are exposed on the ground surface, in a zone

of broken-up rocks with open fractures and fissures and along faults, and also partly from subsurface inflow from deeper water-bearing layers.

There is a regional neotectonically-active formation along the valley of the Lug River, known as the Lužnica-Topčider Fault (PAVLOVIĆ 1980). Near Mladenovac it intersects with the Varovnica Fault, which is also neotectonically active, and a fault structure followed by the valley of the Alinac River. In hydrogeological terms, the Neogene sediments at Selters Banja form a complex of permeable and impermeable strata; Mesozoic flysch strata are largely impermeable, whereas the Lower Cretaceous sediments constitute a permeable lithologic setting of fractured-karst porosity. The highest porosity is found in fault zones, in hard carbonate

rocks and Neogene sediments. The spread of these lithologic settings is deemed to be such that they likely constitute the main region of groundwater circulation.

The mineral water at Sijarinska Banja emerges along a 800 m long linear zone (Fig. 2). The zone features numerous springs at the bottom of a very steep valley of the Banjska River. The water source area, arbitrarily divided into two parts (upper spa and lower spa), originally comprised several shallow wells and one deep well (PROTIĆ 1995; STANKOVIĆ & ZLOKOLICA, 1993; ILIĆ 1988).

The drilling history of the shallow wells began with drinking water supply wells in the alluvions of the Banjska River, which were about 4 m deep. Over time, ordinary and mineral water became mixed. Then, several wells, 9 to 12 m, were drilled through igneous rocks, up to the point of contact with the schists, where the flow was generally artesian. During the course of drilling on the left bank of the Banjska River, an 8 m high gevser erupted. Its water temperature was 71°C. There was another eruption, about 1 m high, from a depth of 12 m, while drilling was taking place near the Main Spring. An 80 m deep well was drilled in crystalline schists with calc tufa interbeds, near the Gejzir Hotel. There was a sudden occurrence of mineral water at 60 m. The rate of pulsating free flow was from 0.06 to 0.18 l/s. A 102 m



Fig. 2. Geological-hydrogeological map of the area of occurrence of mineral water at Sijarinska Banja: 1. alluvial sediments; 2. hydrothermally altered rock; 3. Tertiary igneous rocks; 4. Oligocene sediments; 5. crystalline schists; 6. fault structures (a. Tupale fault zone; b. Banjska River fault zone); 7. drainage zone; 8. recharge zone; and 9. surface water divide.

deep well was drilled in igneous rocks. The water temperature was initially 65 °C, but later dropped to 58 °C. Temperature logging revealed an inversion, from 65 °C in the 15–37 m interval to 56 °C at a depth of 100 m. In the "upper spa", the mineral water is drained via several low-capacity springs (Jablanica, Zdravlje, etc.) and withdrawn from a number of wells whose depths range from 4 to 40 m. After these shallow wells, a deep well was drilled in the "upper spa" through schists, up to a depth of 1232 m. Here the most significant flow rates of mineral water come from tectonic zones at 360 m and 840 m. The shallower tectonic zone delivered 60 l/s of artesian groundwater whose temperature was 77.8 °C, and the deeper zone 33 l/s of artesian groundwater at 72 °C.

The oldest and most widespread rocks in Sijarinska Banja are crystalline schists. They are interspersed with Tertiary igneous rocks. Mineral waters occur within the zone of the Tupale Fault, along the fringes of an igneous mass. This deep fault divides two geotectonic units – Serbian-Macedonian Massif (east) and Vardar Zone (west) (VUKANOVIĆ *et al.* 1973). Judging by data collected on the ground surface, the dip is rather steep to the east and the movement reversed, with a very pronounced displacement component along the trend-

ing direction. Movements along the fault have been intermittent. In the Paleogene, they opened pathways for volcanics. The same movements have continued to the present day. At Sijarinska Banja, on about  $600 \text{ m}^2$ , there is a rather large mass of marbleized onyx adjacent to andesites and crystalline schists. The onyx is believed to have originated from one of the hot springs, which often changed its location due to rapid sedimentation of large masses of aragonite.

According to exploration drilling and mapping along the Banjska River, mineral water emerges from permeable zones at the points of contact between igneous rocks and highly-silicified schists, permeable tectonic zones in the igneous rocks, and open fractures and tectonized zones in the highlysilicified schists.

#### Hydrogeologic structures

The linear distribution of the occurrences of mineral

water in Serbia is a clear indication of their genetic association with tectonic structures, and their (high) permeability is a result of disjunctive neotectonic movements of bordering blocks (MARINKOVIĆ *et al.* 2012). Exploration has shown that a fault zone is the main hydrogeologic structure of a mineral water occurrence (MARINKOVIĆ 2014). It can be deep and very wide, up to 10 km, and can extend for more than 100 km (STEPANOV 1989). Permeable layers of Quaternary and/or Tertiary unconsolidated sediments also constitute hydrogeologic structures of mineral waters in Serbia, where they "screen" fault zones in the solid bedrock.

The main hydrogeologic structure at Sijarinska Banja is the regional fault zone followed by the Banja River Valley. It runs entirely through the solid bedrock (Proterozoic crystalline schists with Tertiary igneous intrusions). Neotectonic activity has maintained and continues to maintain high permeability. There have been intermittent movements during and after ore solution circulation stages (VUKANOVIĆ et al. 1973). In the drainage zone, the fault zone is "screened" by alluvial sediments and marbleized onyx deposits. The spread of these delayed carbonate rocks is an indicator of paleo flows. Drilling of the previously-mentioned shallow wells was accompanied by sudden groundwater discharges after the near-surface lithologic medium, where rapid sedimentation of aragonite had sealed fractures and fissures. The closure of permeable fracture systems, along with the accumulation of a considerable mass of marbleized onyx on the ground surface, caused the points of discharge to move. On this observation scale, the tamping and displacement processes are associated with the ground surface and a small depth below the surface (30-50 m), where carbon dioxide is expected to be released at a given temperature and pressure. The wells at Sijarinska Banja are located along the edge of the hydrothermallyaltered zone, which indicates a connection between earlier circulation of hot solutions and contemporary thermal water flows – as a post-volcanic occurrence. It also seems clear that the paleo and contemporary flows of thermal water have the same heat source.

The southern extension of the fault structure marked by mineral water springs is connected with the main direction of the Tupale Fault (Fig. 2). It is apparent that the trending of the faults reflects a deep fault zone of a certain width, in which the permeable hydrogeologic structure likely spreads along the western side (where there is evidence of paleo circulation of thermal solutions). The drilled permeable tectonized zones, which are distinct at depths of 360 m and 840 m (Figs. 3 and 5), are associated with the deep fault zone and suggest a rather large depth. In the regional fault domain, mineral water circulation at depth is associated solely with these permeable tectonized zones. There is every indication that they comprise a network of highly regular linear zones, which in broad terms belong to the systems that feature a certain spatial orientation. Beyond these bounded permeable tectonized zones the rocks are compact - impermeable.

Mineral water at Selters Banja is formed near the City of Mladenovac, in an area where three neotectonically active tectonic structures cross. The closest is the structure that follows the Alinac River Valley and the other two are regional fault structures known as



Fig. 3. Schematic geological-hydrogeological section through the hydrogeologic structure at Sijarinska Banja: 1. crystalline schist (silicified) with igneous intrusions; 2. recharge zone; 3. drainage zone; 4. zone of dominant subsurface flow;
5. general direction of subsurface flow; 6. direction of carbon dioxide migration; 7. regional drainage base; 8. theoretical depth of the hydrodynamic zone of slow groundwater renewal; 9. theoretical maximum depth of mineral water;
10. compact rock; and 11. hydrodynamic zones: rapid (light gray), slow (gray) and very slow (dark gray) renewal.

the Lužnica–Tupižnica Fault, along the Lug River, and the Varovnica Fault. Wells IB-1 (816.4 m deep) and IB-2 (1150 m) tap mineral water in marly limestones and limestones, from the depth interval of 600 to 1150 m (ČEKIĆ 2013). There are Neogene sediments with permeable and impermeable strata up to a depth of 300 m, largely impermeable Upper Cretaceous flysch from 300 m to 750 m, and further below permeable Mesozoic, slightly-karstified carbonate rocks (Fig. 4).

The first well, after a depth of 239 m, captures mineral water from Sarmatian sediments in the lowest part of the Neogene, and partly also from underlying marly limestones of the Upper Cretaceous (MILOJEVIĆ 1964). The two deep wells tap mineral water in carbonate rocks below the Upper Cretaceous flysch, which are Lower Cretaceous and it appears also partly Jurassic. A relatively small amount is also captured from (overlying) marly limestones and marls of the Upper Cretaceous (flysch). Drilling of the wells did not reveal any tectonized zones. However, it is a fact that this area is situated near the zone where the three previously-mentioned neotectonic structures intersect and that the aquifer is hydraulically linked with the (main) fault zone. Its proximity is indicated by carbon dioxide, which it allows to migrate upward from the depth of origin.

It follows that the fractured-karst aquifer in Mesozoic carbonate rocks is situated on the fringe of the deep fault zone. Thethe fault zone appears to run



Fig. 4. Schematic geological-hydrogeological section through the hydrogeologic structure at Selters Banja (ČEKIĆ 2013; MILOJEVIĆ, 1964, supplemented): 1. Neogene sediments; 2. Lower Neogene flysch; 3. Lower Cretaceous slightly-karstified sediments; 4. Jurassic and Cretaceous flysch; 5. fault; 6. regional drainage base; 7. theoretical depth of hydrodynamic zone of slow groundwater renewal; 8. recharge zone; 9. point of emergence of mineral water; 10. hydrodynamic zones: rapid (light gray), slow (grey) and very slow (dark gray) groundwater renewal; and 11. direction of carbon dioxide migration.

along the Alinac River Valley or (less likely) the Lug River Valley. Based on drilling logs and general geological exploration, the largest amount of mineral water renewed at Selters Banja is associated with slightly-karstified carbonate rocks that underlie the Cretaceous flysch, within the zone of the nearby (as expected), regional, active fault zone.

#### **Distance of recharge zones**

The spread of the hydrogeologic structures is also determined by the distance between the recharge zone and the discharge zone (point of emergence). In the geological-hydrogeological circumstances such as exist at Sijarinska Banja and Selters Banja, these distances were assessed in terms of the spread of the permeable fault zones and the linear distance from the wells to the boundaries of the catchments of surface streams near these two spa towns (Banjska River, Alinac River and Lug River ?). Additionally, the fact that the distance between the recharge zone and the place of discharge needs to be consistent with the determined water age and average flow velocity (per the theoretical velocity for the pertinent permeable lithologic setting) was taken into account.

The mineral waters in the subject hydrogeologic structures are of meteoric origin (PERIĆ & MILIVOJEVIĆ 1990). Atmospheric precipitation is infiltrated directly or indirectly from surface streams and peripheral

water-bearing media. Adjusted to linear structures, the recharge zones acquire the contours of an elongated oval shape. The water age reflects the travel distance from infiltration to discharge and the average flow velocity. In hard rocks, the pathway is determined by the regional, active neotectonic structure. At Sijarinska Banja, the pathway appears to be mapped out by the regional fault of the Banjska River and possibly other faults of a smaller scale (spread, etc.) in the zone of the deep Tupale Fault. At Selters Banja, it is determined by neotectonic faults that cross in this area (fault along the Alinac River Valley, fault along the Lug River Valley – the Lužnica-Topčider Fault and the Varovine Fault).

Given the linear extent of the hydrogeologic structures and the assumed average groundwater flow velocity

 $(1.1 \times 10^{-8} \text{ m/s})$ , the (upstream) distance between the recharge zone and the wells is not greater than 11 km at Sijarinska Banja and 7 km at Selters Banja. However, in view of the fact that in fractured systems groundwater flow does not follow a straight line, these waters travel a much longer distance from the point of entry into to the point of exit from a given water-bearing medium. Looking at only downward and upward travel, it follows that the distance of the recharge zones could also be less than 5 km.

#### Maximum depth of mineral water occurrences

Theoretically, in Serbia's lithosphere mineral water can be found at a maximum depth of 2.5 km, which is determined by the depth of the lithostratigraphic substrates of carbon dioxide (MARINKOVIĆ *et al.* 2013). It is related to the geotectonic unit of the Vardar Zone, where 90% of the registered occurrences of mineral water are located. Recognizing these constraints, the maximum depths of mineral waters at Sijarinska Banja and Selters Banja were determined by examining zones of similar rates of renewal – according to the known hydrodynamic zones of rapid, slow and very slow groundwater renewal.

It is clear that in the case of ascending systems and water age measured in thousands of years, it is not practical to distinguish zones of **rapid groundwater renewal** in the given sense. However, ascending flows of mineral water in the strata closer to the surface can be exposed to lateral infiltration of groundwater from this hydrodynamic zone. Such groundwater causes seasonal variations in water temperatures and discharges of springs and wells. The depth of the occurrences is determined by the regional drainage base. At Sijarinska Banja, the regional drainage base is the Jablanica River (390 m above sea level) and at Selters Banja the Kubršnica River (110 m.a.s.l.). Relative to the recharge zones, which in the case of the considered hydrogeologic structures are located above 500 m.a.s.l. at Sijarinska Banja and above 200 m.a.s.l. at Selters Banja, it follows that the hydrodynamic zones can reach depths greater than 100 m.

Theoretically, the zone of **slow groundwater renewal** lies below the zone of rapid groundwater renewal. Full replacement takes between 100 years and 100 million year (DRAGIŠIĆ 1997). Groundwater movement in this zone is rather slow compared to the zone of rapid renewal. In relatively small artesian basins (Selters Banja), the average depth can be up to 1000 m and in mountainous areas (Sijarinska Banja) up to 2000 m. The natural velocity of groundwater flow is greater than 0.2 m/day or  $6.3 \times 10^{-9}$  m/s.

Deep boreholes (over 1.1 km) clearly indicate that in the considered permeable fault zones the rate of groundwater renewal decreases with depth. At Sijarinska Banja, this was demonstrated while a deep well was being drilled (Fig. 5). From the tectonic zone a yield of about 60 l/s was measured at 360 m, roughly 30 l/s at 840 m, and no flows (water-bearing tectonized zones) were registered down to the ultimate depth of 1150 m.

The highest rate of groundwater renewal at Sijarinska Banja, which corresponds to the zone of slow renewal, occurs at depths between 300 and 1000 m. Thereafter, it gradually declines to below a depth of 1500 m. In this regard, it is fully consistent with the theoretical depth (1000 to 2000 m) in the given mountainous setting. It is obvious that below 1500 m there is a hydrodynamic zone of very slow groundwater renewal.

The mineral water at Selters Banja is captured from the depth interval of 350 to 1150 m (between 200 m and -1000 m above sea level). This interval is entirely in the hydrodynamic zone of slow groundwater renewal (Fig. 6). The thickness of the interval is therefore about 800 m and the highest rate of groundwater renewal traces to the main water-bearing medium -Lower Cretaceous slightly-karstified carbonate rocks. An active fault zone in the vicinity allows the mineral water to move upward from the Lower Cretaceous limestones to the permeable Sarmatian layer (bottom of the Neogene complex of sediments). The waterbearing medium tapped by the deep wells is also recharged from the fault zone. The mineral water has not emerged on the ground surface because this was prevented by impermeable Neogene strata. Obviously, active tectonic movements cannot create a (linear)



Fig. 5. Schematic representation of hydrodynamic zoning (groundwater renewal) at Sijarinska Banja: 1. hydrodynamic zone of rapid groundwater renewal; 2. zone of slow groundwater renewal; and 3. water-bearing tectonized zone.



Fig. 6. Schematic representation of hydrodynamic zoning (groundwater renewal) at Selters Banja: 1. zone of rapid groundwater renewal; 2. zone of slow groundwater renewal; 3. zone of very slow groundwater renewal; 4. aquifer.

permeable zone through these strata. It follows that the main aquifer of mineral water in the Lower Cretaceous carbonate rocks is recharged and drained along the linear zones of active neotectonic movements, that the depth of the zone of slow groundwater renewal depends on the depth of these carbonate rocks and the permeable fault zone, and that the recharge zone must be on or beyond the Neogene fringe. The zone of **very slow groundwater renewal** is at depths greater than 1000m/2000m. The natural rate of groundwater flow is very low (less than 0.05–0.1 m/year). Consequently, the end of the zone of slow and the beginning of the zone of very slow groundwater renewal at Sijarinska Banja is to be expected in the depth interval of 1.5 to 2.0 km, and in the case of Selters Banja below 1.3 km.

It follows that the largest amount of groundwater in the considered hydrogeologic structures is restored in the hydrodynamic zone of slow groundwater renewal.

#### Conclusion

The spread of the considered hydrogeologic structures could only be assessed in general, to an extent that in regional terms provides a sufficiently clear picture of the expanse, distance of recharge zones and depths of the studied occurrences of mineral waters.

The lowest average rates of groundwater flow  $(1.1 \cdot 10^{-8} \text{ m/s})$  were determined on the basis of the distance of the surface water divides, water age, and theoretical velocities in analogous fractured settings. Considering all the above and the fact that in fractured aquifers groundwater travels much longer than the linear distance from the point of infiltration to the point of discharge (descending and ascending pathways, meandering flow in 3D space), the conclusion is that this distance at Selters Banja can be from less than 5 km to not more than 7 km, and at Sijarinska Banja from less than 5 km to a maximum of 11 km.

The highest rate of groundwater renewal in the studied hydrogeologic structures occurs within the known hydrodynamic zone of slow groundwater renewal, and the generation and migration of carbon dioxide in the zone of very slow groundwater renewal. At Sijarinska Banja, this happens at depths up to 1.5 km and there is a gradual decrease with depth. Below this depth and down to 2 km, there is a boundary between the zone of slow and the zone of very slow groundwater renewal. At Selters Banja, mineral water is captured from the depth interval of 360 to 1150 m, and the highest rate of groundwater renewal occurs below a depth of 800 m, associated with slightlykarstified carbonate rocks. The depth of the mineral water in this spa town is determined by the depth and permeability of the rocks and neotectonically active faults. Drilling has not revealed a tectonized zone but the proximity of active regional fault structures and the presence of carbon dioxide gas clearly indicate that it is close and that there is a hydraulic link with the encountered water-bearing media in marly and slightly-karstified carbonate rocks (in the depth interval of 360 to 1150 m). In the hydrogeologic structure at Selters Banja, the boundary between the hydrodynamic zones of slow and very slow groundwater renewal is below a depth of 1.3 km.

The identification of regional fault zones where mineral waters are formed and renewed, the distance of the recharge and drainage zones, and the depth of the mineral water facilitate efficient hydrogeologic exploration for the purposes of increasing water source capacity, locating thermal groundwater, and addressing other specific tasks.

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#### Резиме

#### Хидрогеолошке структуре Сијаринске Бање и Младеновачке "Селтерс" бање

Циљ овог рада био је да се на примеру једне од старијих (Сијаринска б.) и једне од млађих ("Селтерс" б.) угљокиселих минералних вода Србије дефинишу границе пространства хидрогеолошких структура у којима се оне формирају. Истраживања су показала да се основном хидрогеолошком структуром ових вода може сматрати разломна зона (Маринковић 2014). Познато је да оне буду велике ширине, и до 10 km, пружања и преко 100 km и дубоког залегања (Степанов 1989). Хидрогеолошке структуре угљокиселих минералних вода Србије су и водопропусни слојеви квартарних и /или/ терцијарних невезаних седимената, тамо где они "екранирају" разломне зоне угљокиселих вода у чврстим стенама геолошке основе. У Сијаринској бањи угљокиселе воде су истицале природним путем, док су у "Селтерс" бањи оне откривене случајно, будући да се нису испољавале на површину терена.

Старост вода је у сагласности са дужином путање коју вода пролази од момента инфилтрације до момента истицања и просечном брзином тока. У чврстим стенама њихова путања је на тој дужини "трасирана" регионалном активном неотектонском структуром. За Сијаринску бању, ова путања је предиспонирана регионалним разломом Бањске реке и евентуално другим разломима мањих размера (пружања и др.) у домену дубоког тупалског разлома. За термоминералне воде Младеновачке "Селтерс" бање то се односи на неотектонске раседне структуре које се на овом подручју укрштају (расед долином реке Алинац, долином реке Луг Лужничко-топчидерски расед и Варовнички расед).

Угљокиселе воде су атмосферског (инфилтрационог) порекла (ПЕРИЋ & МИЛИВОЈЕВИЋ 1990). Атмосферске падавине се инфилтрирају директно или индиректно преко површинских токова и граничних водоносних средина. Прилагођене линијским структурама, области прихрањивања задобијају контуре издуженог овалног облика. Узимајући у обзир линијско пружање хидрогеолошких структура и усвојену просечну брзину подземних вода у њима, од  $1,1 \cdot 10^{-8}$  m/s, добија се да је област прихрањивања за хидрогеолошку структуру Сијаринске бање од изворишта удаљена (узводно) највише 11 km, а за "Селтерс" бању 7 km. Међутим, будући да у пукотинским системима подземни ток не може да има праволинијску путању, јасно је да воде прелазе далеко дужи пут у односу на праволинијско растојање од места уласка до места истицања из датих водоносних средина. Ако се рачуна само дужина силазне и узлазне путање, произилази да разматране удаљености области прихрањивања могу да буду и мање од 5 km.

У раду је показано да се дубина досезања инфилрационих вода у водопропусним разломним зонама може сагледати и анализом дубина њихове циркулације у односу на познате хидродинамичке зоне (интензивних, успорених и веома успорених процеса водозамене). Теоретски, у литосфери Србије угљокиселе воде могу да досежу максимално до 2,5 km дубине, односно до дубине коју одређује дубина залегања литостратиграфских супстрата угљендиоксида (Маринковић *и др.*, 2013).

За област Сијаринске бање регионални дренирајући базис представља река Јабланица (390 m надморске висине), а за област "Селтерс" бање река Кубршница (110 m надморске висине). У односу на области прихрањивања, које се код разматраних хидрогеолошких структура налазе на надморској висини изнад 500 m за Сијаринску бању, односно изнад 200 m за "Селтерс" бању, произилази да у њима хидродинамичка зона интензивних процеса водозамене може да досеже до дубине веће од 100 m.

У раду је закључено да се главна количинска измена у разматраним хидрогеолошким структурама одвија у домену познате хидродинамичке зоне успорених процеса водозамене, а генерисање и миграција угљендиоксида у домену зоне веома успорених процеса водозамене. Постигнути резултати дубоким бушотинама, преко 1,1 km дубине, јасно указују да се у предметним водопропусним разломним зонама са дубином смањује количинска измена подземних вода (интензивност водозамене). У Сијаринској бањи она се јасно испољила при бушењу дубоке бушотине. Из тектонске зоне на 360 m измерена је издашност око 60 l/s, на 840 m око 30 l/s, а од 840 m до крајње дубине 1150 m, приливи нису регистровани (водоносне тектонски изломљене зоне). За Сијаринску бању највећа количинска измена одвија се до 1,5 km ду-

бине, са тенденцијом поступног смањивања са дубином. Испод ове, а до највише 2 km дубине, налази се граница између хидродинамичке зоне успорених и веома успорених процеса водозамене. Код "Селтерс" бање угљокиселе термоминералне воде су захваћене у интервалу од 360 до 1150 m дубине, а главна количинска измена ових вода одвија се испод 800 m дубине и везана је за слабо карстификоване карбонатне стене. Дубина досезања вода ове бање условљена је дубином залегања и водопропусношћу ових стена и неотектонски активних разлома. Тектонизирана зона није набушена, али близина активних регионалних раседних структура и постојање гаса угљендиоксида, јасно указују на њихову близину и хидрауличку везу између њих и набушених водоносних средина у лапоровитим и слабо карстификованим карбонатним стенама (у интервалу 360–1150 m дубине). За хидрогеолошку структуру "Селтерс" бање граница између хидродинамичке зоне успорених и веома успорених процеса водозамене налази се испод 1,3 km дубине.

Дефинисањем пространства регионалних разломних зона у којима се угљокиселе воде формирају и обнављају, удаљености области прихрањивања од изворишта и дубине досезања угљокиселих вода, омогућавају се рационалнија и ефикаснија хидрогеолошка истраживања – за потребе повећања издашности изворишта, изналажења вода виших температура и решавања других конкретних задатака.

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## Hydraulic characterization of laterals as applied to selected radial collector wells at Belgrade Groundwater Source

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Abstract: The paper examines the possibility of hydraulic characterization of radial well laterals in a manner that does not require prior hydrodynamic analysis by simulating groundwater extraction conditions on a numerical model. The first step of the proposed approach is to assess the groundwater level regime formed in the capture zone when the well is operating, which is indicative of the functional condition of the laterals and the aquifer potential in terms of groundwater availability. Then the efficiency of the laterals is examined through the hydraulic function of the skin zone, depending on its filtration properties. An expression for groundwater flow from the aquifer to the laterals (commonly used to simulate laterals on a hydrodynamic model) is employed to define representative values of the conductance coefficient of the skin zone (as an indicator of colmation), and then applied to several wells at Belgrade Groundwater Source. The present research shows that a conductance coefficient of  $[K_s/d_s]=1.0\times10^{-4} \text{ s}^{-1}$  can be considered as the threshold value in relation to which the effects of colmation of well laterals are exhibited, which is consistent with the results reported by researchers who studied the effect of skin zone conductance on the occurrence and nature of the so–called early drawdown at radial collector wells. In addition to gaining insight into the present condition of the laterals, the proposed approach can be used to study the progress of colmation at different points in time and to quantify the effectiveness of regeneration of laterals.

Key words: radial collector well, groundwater level regime, skin zone, conductance coefficient.

Апстракт: Циљ рада је сагледавање могућности дефинисања хидрауличких карактеристика дренова на начин који не подразумева претходну израду хидродинамичке анализе симулацијом услова експлоатације подземних вода на нумеричком моделу. Први корак у предложеном приступу представља анализа режима нивоа подземних вода који се формира у непосредној зони и под утицајем рада бунара, а који указује на функционално стање дренова и потенцијал водоносне средине у погледу расположивих количина подземних вода. У наставку се анализира ефикасност дренова преко хидрауличке функције прифилтерске зоне, у зависности од њених филтрационих својстава. Преко израза за дотицај воде из издани у дренове (којим се најчешће симулирају дренови на хидродинамичким моделима), дефинисане су репрезентативне вредности коефицијента пропусности прифилтерске зоне (као показатеља њихове колмираности) на примеру више анализираних бунара београдског изворишта подземних вода. Спроведено истраживање указује да се вредност коефицијента пропусности дренова од [K<sub>приф</sub>/d]=1,0×10<sup>-4</sup> s<sup>-1</sup> може сматрати граничном вредношћу у односу на коју се испољавају ефекти колмираности дренова, што је у сагласности са резултатима истраживања аутора који су испитивали утицај пропусности прифилтерске зоне на појаву и карактер тзв. раног снижења код хоризонталних бунара. Осим упознавања актуелног стања дренова, представљеним приступом се може пратити напредовање процеса колмирања дренова у различитим временским тренуцима, као и квантификовати ефекти регенерације дренова.

**Кључне речи:** бунар са хоризонталним дреновима, режим нивоа подземних вода, прифилтерска зона, коефицијент пропусности дрена.

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## Introduction (present condition of the wells and current extraction rate)

Belgrade Groundwater Source (BGWS, Fig. 1) is currently comprised of 99 radial collector wells and 47 tube wells. The radial collector wells contribute more than 90% to the BGWS output.

Well ageing is a process that has accompanied groundwater extraction since the very beginning, from the early 1950s (DIMKIĆ *et al.* 2011a, DIMKIĆ *et al.* 2011b, POLOMČIĆ 2000). Over time, the condition of the laterals of the radial collector wells has deteriorated and reduced well discharge. The needed amount of drinking water has been provided by continuous lowering of the water level inside the well caissons (i.e. by intensifying production). Occasional mechanical regenerations of the laterals were undertaken in an attempt to decelerate the discharge decline. In the past decade, despite regenerations, a sustained downward trend has been about 100 l/s per year.

ence of the Sava and the Danube), which is a stage of 95% exceedance probability. These hydrologic conditions resulted in a record low rate of groundwater extraction by the radial collector wells – only about 3 m<sup>3</sup>/s. Consequently, the water levels inside the caissons were extremely low and in the 96 active wells they were 4.75 m above the laterals, on average. The greatest drawdown was recorded in the caisson of well RB–28, where the water column was only 1.0 m above the laterals.

During the period of low flows of the Sava River, the average discharge of the wells was about 30 l/s. The discharge of 20% of the wells was less than 10 l/s and that of another 20% greater than 60 l/s. The discharge of only three wells was above 100 l/s.

The condition of the laterals is such that out of about 800 laterals in place, one-third had been out of commission for a relatively long time due to major damage to the screen pipes and loss of the water capture function. One third of the laterals had been short-



Fig. 1. Geographic location of Belgrade Groundwater Source.

During a period of low flows of the Sava River (from mid-July to mid-August 2015), the river stages were generally below an elevation of 70 m above sea level (at a Belgrade gauging station near the confluened, damaged, filled with material from the nearscreen zone and vertically displaced. As a result, the length of only one third of all the laterals is close to the initial length. The condition of these laterals was
considered good, despite the fact that some of them were colmated (i.e. clogged). The lowered capture capability had been addressed by regeneration.

The condition of the wells and the rate of groundwater extraction, as described above, necessitate systematic rehabilitation of the BGWS wells, which would need to include nearly half of the wells in the immediate future. Objectively, 4–5 wells can be revitalized per year, such that rehabilitation would take an entire decade. In the meantime, the condition of a number of wells whose current discharge capacity is above average would deteriorate and they, too, would require replacement of laterals. As such, similar to past regenerations, replacement of laterals might become an ongoing activity in the future, to ensure a consistent water supply.

#### Criteria for selecting wells to be rehabilitated

The selection and ranking of "candidate" wells for rehabilitation cannot be based solely on the current condition of their laterals. The conclusion that the laterals of a well are not functioning and that there is a dramatic loss of discharge does not constitute a sufficient basis for undertaking the design of the installation of new laterals and procuring the needed funding.

In addition to knowing the condition of a well, it is essential to understand the main natural features and aquifer recharge conditions in the capture zone. Only such an approach is warranted for addressing the present state of affairs at BGWS and selecting wells where it would be justifiable, in technical and economic terms, to emplace new laterals and ranking the wells based on the expected increase in discharge capacity.

Even when a well is properly designed and built, if the potential of the well site is modest, new laterals will not bring about significant improvement in terms of capacity increase ( $\Delta Q$  in the design). Another well will have to be revitalized to ensure a sufficient amount of drinking water. In other words, even though the money spent will only partially justify the outcome, spending will have to be repeated (i.e. doubled).

Past rehabilitations of laterals at BGWS (six wells in 2005–2009 and one well in early 2016) have shown that this activity requires considerable funding and that the spending per well is generally the same. In view of the fact that the BGWS aquifer is highly heterogeneous in terms of groundwater availability at different well sites, the outcomes of laterals replacement can result in diverse well discharges (as corroborated by experience).

BGWS well rehabilitation priority needs to be given to the wells and sites with a high potential for achieving significant discharge capacities. The approach is based on two objectives: (i) to first halt the downward production trend (already quite alarming), and (ii) to then increase and maintain the rate of groundwater extraction at the needed level.

The most important information needed for well rehabilitation design is as follows:

- Well: elevation of emplacement, number and condition of active laterals; operational history and effectiveness; operating water levels; and effects of any past rehabilitations;

- Geologic framework and hydrogeological features: lithostratigraphic composition and grain-size distribution of the deposited clastic sediments; groundwater flow characteristics; and geometry of riverbed incision into the aquifer;

- Hydrodynamic conditions: quality of hydraulic contact between the river and the aquifer; rates of recharge from the river and the hinterland; aquifer regime; and local hydraulic losses at the lateral screens (according to DIMKIĆ *et al.* 2011b, DIMKIĆ & PUŠIĆ 2014);

 Hydrochemical and microbial composition of the groundwater: iron and dissolved oxygen concentrations; redox potential; and activity of certain bacterial species.

Such information is collected by means of various types of investigations and analyses.

The amount of groundwater captured by a well is a function of the permeability of the sediments (all lithostratigraphic layers in the vertical section of Quaternary sediments, not only that or those in which the laterals are installed), recharge conditions of the medium through which groundwater flows under the influence of the operating well, technical characteristics, the condition of the water–capturing parts of the well, the operating mode, and the like.

Regardless of the current capacity of a radial collector well, production causes the formation of a certain dynamic groundwater level in the zone of influence. The surface of the groundwater level in the capture zone is typically three-dimensional. Given the present number and condition of the laterals, the groundwater levels in the vicinity of BGWS wells exhibit a distinct spatial irregularity.

Gauging of well discharge and water levels in the caisson, ascertaining of the current condition of the laterals (by underwater video recording, including determination of vertical displacement), analyses of the chemical and microbial composition of a number of parameters, and installation of 2–3 suitably located piezometers, along with regular groundwater level monitoring, constitute an adequate scope of investigations for gaining insight into the status of each well and the potential of the well site. Once wells are selected in this manner for the rehabilitation of laterals, subsequent investigations (hydrodynamic simulation of regime conditions monitored over a longer period of time) will provide more detailed insight into pertinent conditions.

The approach outlined above improves the efficiency of the investigations, as well as cost–effectiveness, given that each activity of this type requires funding which, in reality, is not always easy to procure. Uniform BGWS coverage by these investigations is equally important, in view of the fact that the information required for the rehabilitation design for some wells has been available for years, while for others the lithological composition of the setting or the piezometric head is still unknown.

# Assessment of the groundwater level regime as a criterion for prioritizing well rehabilitation

Assessment of the groundwater level regime provides needed information, for example, whether the potential capacity of the well site is modest or considerable and if the filtration characteristics of the water-bearing medium are relatively unfavorable, sound or very good. For a preliminary selection of wells, it is not necessary to know whether a modest potential is a result of the lithologic stratification, presence of semi-permeable interbeds, anisotropy, reduced recharge from the direction of the river, influence of neighboring wells, or the like. These details are explored through subsequent investigations, in the well rehabilitation design phase (and after all the wells that have a greater potential for achieving high discharge rates have been revitalized). Or, to select the wells to be rehabilitated, it is enough to know whether the laterals are incrusted and, of so, to what extent. Subsequent activities will determine whether the encrustations are largely mechanical or biochemical in nature.

An integrated functional analysis of the radial collector well and the water–bearing medium will constitute a basis for:

 decision-making regarding the activities that need to be undertaken to improve the condition of the well and the entire groundwater source,

– ensuring that the selection allows for the considerable funding needed to first be spent on wells where high discharge rates are achievable, to halt the downward production trend and provide proper water supply for Belgrade, and then tackle the other wells where satisfactory and consistent discharges can be achieved (in other words, reduce the risk of limited or negative results),

 a preliminary but objective assessment of the site/groundwater resource, and prediction of the effectiveness of new laterals (post-rehabilitation discharge capacity, assuming that the work is done properly), and

- defining local hydraulic resistances at the laterals, as well as hydraulic characteristics of existing laterals (skin zone).

# Hydraulic characterization of laterals

The conductance coefficient of a lateral, or its resistance coefficient,  $[K_s/d_s]$ , is an extremely important

parameter for assessing operating conditions of a radial collector well. It indicates the effectiveness of the lateral and the extent of its hydraulic function (which enables groundwater extraction), or if it is closed due to colmation, improper emplacement or development, or the characteristics of the screen pipe and gravel pack (which actively hinder its function). In this regard, the hydraulic role of the skin zone, or the so-called *skin effect* (FENG & ZHAN 2016, YEH & CHANG 2013, PASANDI *et al.* 2008, YEH & YANG 2006, BARRASH *et al.* 2006, KAWECKI 2000), can either be negative or positive.

The conductance coefficient of a lateral is obtained by defining the filtration characteristics of the skin zone (representative hydraulic conductivity), even though it in essence reflects the extent of the hydraulic resistances at the lateral screen and its skin zone. Quantification of this parameter over time demonstrates the progress of well ageing.

A precondition for defining the conductance coefficient of a lateral, as an indicator of its efficiency, is the presence of a piezometer (with a short screen, up to 1 m, installed at the same depth as the lateral), which should be located as close as possible to the lateral (at a distance of up to 1 m). Clearly, piezometer bores need to be drilled very carefully, so as not to damage the lateral (as a rule, the horizontal displacement of a lateral is unknown but reasonably assumed to exist).

It is desirable to perform measurements to determine the capacities of individual laterals in operation (by placing a current meter at the beginning of the lateral), as this method can be used to determine the conductance coefficient for each of the active laterals of a radial collector well. Otherwise, approximate capacities of the laterals can be derived from the correlation between well discharge and the number of functional laterals, along with an analysis of the groundwater level as an indicator of the rate of groundwater extraction.

If an adequate observation well is in place, the conductance coefficient of a lateral can be determined from the expression used for simulating the boundary condition "radial well lateral" in contemporary hydrodynamic analyses, or by mathematical modeling of groundwater flow under the influence of a radial collector well (Božović *et al.* 2015, DIMKIĆ *et al.* 2011c, LEE *et al.* 2010, MOHAMED & RUSHTON 2006, BAKKER *et al.* 2005, PARK & ZHAN 2002):

where:

$$2r\pi L = \omega$$
 and  $[K_s/d_s](H_{NP} - H_{RW}) = v$ 

 $q = 2r\pi L [K_s/d_s](H_{NP} - H_{RW}) [1]$ 

and where:

q is the flow to a single lateral  $(m^3/s)$ ;

r is the flow to a single lateral  $(m^{3}/s)$ ;

L is the actual or assumed length of the lateral (m);  $K_s$  is the hydraulic conductivity of the skin zone (m/s);

 $d_s$  is the thickness of the skin (colmated) zone (m);

H<sub>NP</sub> is the groundwater level at the neighboring piezometer (m.a.s.l.);

 $H_{RW}$  is the water level in the caisson (m.a.s.l.);  $\omega$  is the surface area of the screen pipe (m<sup>2</sup>); and

v entrance velocity to the lateral (or approach velocity; occurs at the contact/contour between the skin zone and the screen (m/s)

Note: The approach velocity is Darcy's velocity, not the actual groundwater flow velocity in the analyzed zone adjacent to the screen. The actual groundwater flow velocity in the skin zone (generally assumed and calculated as the mean linear velocity), is obtained from the relation of inflow rate into the lateral and the porosity of the skin.

It is evident that hydraulic characterization of a lateral involves defining of the hydrogeological function of the skin zone, or the measure in which it acts as a on account of infiltration of surface water, and whose filtration properties are poorer than those of the aquifer sediments with which they are in physical contact (LEE *et al* 2010, SUN & ZHAN 2006, POLOMČIĆ 2001). As a result, the formation of a skin zone around the laterals, whose filtration properties are poorer, as a rule, has an adverse effect on the operation of the well.

Presented below is the definition of the conductance coefficients of the laterals of the representative wells selected for analysis of characteristic groundwater level regimes in the BGWS well region, as well as a comparison of the results to the outputs of detailed hydrodynamic models (Božović *et al.* 2016).

The first example is well RB–7m (hydrogeological cross-section in the vicinity of the well is presented in figure 2), which has four open laterals whose condition is rather poor (damaged screens filled with aquifer material). They are also colmated, as evidenced by a



Fig. 2. Hydrogeological cross-section in the vicinity of the well RB-7m.

barrier to the infiltration of groundwater from the aquifer into the lateral. According to Darcy's law, the intensity of groundwater exchange between the aquifer and a lateral (of certain length and diameter), contrary to the difference in piezometric head between the inside and the immediate outside of the lateral, is a function of skin zone conductance. The piezometric head difference along the way through the skin zone can be defined as local drawdown, or local hydraulic resistance (DIMKIĆ & PUŠIĆ 2014).

The hydraulic "origin" and function of the skin zone sediments are analogous to those of the riverbed deposits, which determine the rate of aquifer recharge low discharge capacity, low/reduced operating water level in the caisson and high groundwater level in the zone of the laterals. The lateral which is practically filled–up over its entire cross-section at the caisson wall can be assumed not to take part in groundwater extraction. Based on groundwater level regime analysis, a uniform drawdown at the piezometers in the well zone suggests that the individual capacities of the laterals are nearly the same. Their common feature – poor condition – supports the assumption of equivalent capacity.

Applying Eq. [1] to the regime conditions that existed on 27 February 2014, for example, when the gauged capacity of the well was Q=20 l/s (q $\approx$ 6.65 l/s), the

water level in the caisson  $H_{RW}$ =55.88 m.a.s.l. and the groundwater level at piezometer RB-7m/P-3 (located between active laterals 1 and 2) at  $H_{NP}$ =68.15 m.a.s.l., assuming that the laterals had retained most of their initial length, the resulting hydraulic conductance was  $[K_s/d_s]=2.6\times10^{-5}$  s<sup>-1</sup>. The value obtained in this manner was similar to that derived by simulating groundwater extraction conditions on a detailed hydrodynamic model (Božović *et al.* 2016):  $[K_s/d_s]=2.5\times10^{-5}$  s<sup>-1</sup>.

Given that in many cases it is not possible to determine the length of the laterals, their hydraulically-active lengths need to be assumed. This means that calculations are based not only on an assumed capacity of the lateral, but also its assumed length, which increases the error of the results. In such a case it is more reasonable to follow a different approach and define the representative value of all active laterals via the known capacity of the well, rather than for each of the laterals. This approach is applicable only if the piezometers record roughly equal dynamic groundwater levels of the aquifer. Therefore, Eq. [1] acquires the form:

$$Q = 2r\pi L_{tot} [K_{r.s}/d_s](H_{NP} - H_{RW})$$
 [2]

where  $\omega$  becomes:  $2r\pi L_{tot} = \omega_{tot}$ 

and where:

Q is the discharge capacity of the well  $(m^3/s)$ ; L<sub>tot</sub> is the total length of active laterals (m);

 $K_{r.s}$  is the representative hydraulic conductivity of the skin zone of the active laterals (m/s); and

 $\omega_{tot}$  is the total capture surface of the active laterals (m<sup>2</sup>).

The second example is well RB-42, which has been exhibiting the effects of colmation in the past dozen years, since the last rehabilitation of its laterals in 2004. Unfavorable hydrochemical conditions and the production and maintenance history of this well indicate that its capacity has steadily declined since it was placed online. Given that the laterals were exposed to incrustation, the effects of this phenomenon in terms of a declining conductance coefficient of the skin zone were analyzed at two points in time, three years apart.

At the beginning of November 2011, the water level in the caisson was at  $H_{RW}$ =53.80 m.a.s.l., which resulted in a discharge capacity of Q=21.6 l/s. Due to operation in this mode, the groundwater level at piezometer Prb-42-1 was at  $H_{NP}$ =62.23 m.a.s.l. The total length of three laterals, which had retained most of their initial lengths, was  $L_{tot}$ =125 m. Under such conditions, the conductance coefficient of the laterals (conductance of the skin or the coefficient of colmation of the laterals), was  $[K_{r,s}/d_s]$ =3.25×10<sup>-5</sup> s<sup>-1</sup>.

Three years later, at the end of October 2014, the following was established: well discharge capacity Q=13.6 l/s, water level in the caisson  $H_{RW}$ =55.49 m.a.s.l., groundwater level at piezometer Prb-42-1  $H_{NP}$ =67.06 m.a.s.l., and the length of the laterals unchanged. The capture capability of the laterals during the analyzed period dropped to  $[K_{r,s}/d_s]$ =1.50×10<sup>-5</sup> s<sup>-1</sup>. As such, the change in the conductance coefficient of the laterals corroborated that the discharge capacity of the well declined as a result of colmation and, consequently, the groundwater levels in the well zone rose.

This approach of comparing calculated values at two points in time is also applicable to assessments of the effectiveness of mechanical rehabilitation of laterals.

Hydraulic losses at the laterals are only one (timevariable) part of the total losses during groundwater flow influenced by the operation of a well (from the contour at a certain distance from the well, where the impact of production ceases, to the point of entry into the screen pipe). Analyses of the groundwater level regime in the zone of the BGWS well laterals showed that if the filtration characteristics of the lateral skin zone did not differ considerably from the representative hydraulic conductivity of the lithostratigraphic layer in which the laterals were emplaced, the losses in the skin zone had no major effect on the occurrence of additional resistances and, as such, they had no substantial effect on the operating conditions of the well. This meant that the skin zone, as a thin layer which hydraulically separates the lateral from the water-bearing layer and whose conductance coefficient is lower, according to PARK & ZHAN (2002), essentially did not exist. Such conditions are present initially, after a successful mechanical regeneration of old laterals, when the characteristics of the new laterals are well suited to the porous medium, as well as in the case of existing laterals with no visible signs of incrustation.

PARK & ZHAN (2002) proposed a certain threshold value, based on a sensitivity analysis of drawdown (so-called early drawdown, immediately after the well is placed online), depending on the conductance coefficient of the skin zone on a hypothetical model. Their research showed that at a hydraulic conductivity of the skin zone greater than  $[K_s/d_s]=1,0\times10^{-4} \text{ s}^{-1}$ , the skin effect may be disregarded.

To assess the performance of wells under real BGWS conditions, it is important to determine whether the said value is appropriate and if Eqs. [1] and [2] can be used to establish the hydraulic conductivity of the porous, water-bearing medium. Hydraulic characterization of the laterals that are not (or not considerably) exposed to colmation is presented using wells RB-46 and RB-8m as examples.

The analysis of hydraulic characteristics of well RB-46 was conducted under the conditions that existed in April 2012. The conditions were: well discharge capacity Q=21.0 l/s, water level in the caisson  $H_{RW}$ =55.22 m.a.s.l., groundwater level at piezometer RB-46/P-1 (which registers the lowest levels) at  $H_{NP}$ =59.94 m.a.s.l., and assumed length of the screen

section of lateral No. 8 L=20 m. In these conditions, the conductance coefficient of the studied lateral was  $[K_s/d_s]=1.35\times10^{-4} s^{-1}$ . It is similar to the value obtained from hydrodynamic model tests:  $[K_s/d_s]=1.25\times10^{-4} s^{-1}$  (Božović *et al.* 2015). The representative hydraulic conductivity of the layer in which the laterals are emplaced in the zone of well RB-46 was calibrated on the model to K=1.0×10<sup>-4</sup> m/s.

The last example is well RB-8m. The water level in the caisson has for years been maintained at about 53.20 m.a.s.l. (Fig. 3), meaning 4 m above the laterals. It was evident that the operating water level in the caisson was very low and that the well was under stress. As a result, the achieved well discharge has been 35–40 l/s (Fig. 4). After regeneration in January 2012, four open laterals remained. Underwater filming revealed that the length of the screen pipes was 165 m (i.e. that the original length was retained). The condition of the screens was found to be rather poor.

When the water level in the caisson was low, the groundwater levels in the vicinity of the well, monitored by three piezometers, were at different depths (Fig. 3). Of course, the registered groundwater levels



Fig. 3. Groundwater levels in the zone of well RB-8m.



Radial Collector Well RB-8m

Fig. 4. Discharge capacity of well RB-8m.

are a function of the distance between the piezometers and the laterals, as are the capture rates of the laterals.

Figure 3 shows that at the end of 2012, as the stages of the Sava River increased, the conditions were such that the structural properties of the laterals were affected to the extent that they could not withstand them and collapsed. As expected, this reduced the discharge capacity of the well, which has since been on the decline. This was the reason for selecting October 2012 for the conductance coefficient analysis, given that it was the last time the conditions were representative before the regime changed.

The piezometric head at observation well RB-8m/P-1, which registered the lowest levels and which was located adjacent to lateral No. 3, had fluctuated over a long period of time between 55 and 56 m.a.s.l. As a result of the ultimate phase of degradation of the lateral, which began at the end of 2012, the groundwater level steadily rose (up to 62.5 m.a.s.l.).

Under the October 2012 conditions, the 2 m difference between the water level at piezometer RB-8m/P-1 and that in the caisson indicated that the lateral was hydraulically open (i.e. not very colmated). Otherwise,

> it would not have been able to achieve such a large drawdown relative to the quasi-static level (about 12 m), and could not have been a notable contributor to the summary discharge of the well. That the lateral was not colmated was corroborated by the fact that the piezometric head at the well site had not substantially changed (< 1 m), nor did the discharge capacity of the well ( $\Delta Q \approx 5$  l/s at the same operating water level).

> The calculation parameters were: Q=39.0 l/s, caisson water level  $H_{RW}$ =53.30 m.a.s.l., groundwater level at piezometer RB-8m/P-1  $H_{NP}$ =55.30 m.a.s.l., length of screen section of lateral #3 L=45.6 m, and discharge capacity of the lateral unknown and therefore assumed.

> The status at the other piezometers was analyzed to estimate the discharge capacity of the lateral. The groundwater level at piezometer RB-8m/P-2, which is located adjacent to the very edge of the river and between open laterals #1 and #2, indicated that their postregeneration discharge capacity had not considerably altered. The groundwater level at pie

zometer RB-8m/P-3, located immediately beyond the well caisson, indicated that it was the least affected by production (recorded the highest levels).

For hydraulic characterization of lateral #3, it was assumed that its contribution to the overall gauged well discharge was q $\approx$ 15 l/s. The conductance coefficient of this lateral was therefore [K<sub>s</sub>/d<sub>s</sub>]=2.6×10<sup>-4</sup> s<sup>-1</sup>.

In view of the supposed discharge capacity of the lateral, it was assumed that the representative hydraulic conductivity of the medium in the well zone was not greater than  $K=4.0\times10^{-4}$  m/s. Otherwise, there could not have been considerable lowering of the groundwater level, which was present on the contour of the lateral as a result of groundwater filtration through the porous medium of modest filtration characteristics.

# Conclusions

The actual condition of the wells at Belgrade Groundwater Source is such that the discharge capacity of half of the radial collector wells can only be recovered by installing new laterals and it is therefore extremely important to prioritize the order of rehabilitation.

The groundwater level regime in the zone of the well is an indicator of the functional condition of the laterals and the potential of the water-bearing medium in terms of groundwater resources. Analysis of the regime is a prerequisite for gaining insight into the condition of the laterals, by defining the hydraulic function of the skin zone.

The results obtained using the proposed approach, compared to the results of previous research on detailed hydrodynamic models, indicate that the hydraulic characteristics of the laterals can be quantified with a degree of reliability sufficient to analyze and monitor the actual condition to the wells, as well as to make a preliminary selection of wells to be rehabilitated.

It was established that by defining the conductance coefficients of the laterals at different points in time, it is possible to monitor the progress of colmation, which is a basis for predicting any further decline in capacity or estimating conditions that will require maintenance (e.g. regeneration of laterals). In addition, the value of this parameter before and after regeneration can serve as a suitable indicator for a quantitative assessment of the effectiveness of regeneration.

The results showed that there was a good match between the threshold value of the horizontal well skin conductance of  $[K_s/d_s]=1.0\times10^{-4} \text{ s}^{-1}$ , proposed by PARK and ZHAN (2002), and coefficient of colmation of laterals of the BGWS radial wells, and that it can therefore be accepted. In cases where the conductance coefficient of the skin zone was less than the declared value (e.g. wells RB-7m and RB-42), the effects of incrustation were evident. Where the filtration properties of the skin zone were better than proposed (e.g. wells RB-46 and RB-8m), their impact on the operation of the wells and groundwater extraction were practically negligible. In that case, the hydraulic conductivity of the water-bearing medium (the lithostratigraphic layer in which the laterals are emplaced) can in principle be considered equivalent to the hydraulic conductivity of the skin zone.

The obtained values need to be verified and the hydraulic efficiency of the laterals analyzed further in the design of an optimal solution for the rehabilitation of the laterals of the selected wells. This will be accomplished by developing a detailed hydrodynamic model, to verify or additionally calibrate the initial hydraulic conductivity of the medium, estimated on a preliminary basis via the hydraulic characteristics of non-colmated laterals.

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## Резиме

### Дефинисање хидрауличких карактеристика дренова на примерима бунара београдског изворишта подземних вода

Функционално стање дренова данас има доминантан утицај на капацитет бунара београдског изворишта подземних вода. Стање филтерских цеви и хидрауличке карактеристике прифилтерске зоне су основни разлог значајног снижења нивоа у шахтовима бунара и скромних капацитета бунара. Узрок оваквог стања је процес старења, који представља појаву која прати експлоатацију подземних вода на изворишту од самог почетка изградње овог типа водозахватних објеката, почетком педесетих година прошлог века.

Током времена експлоатације, на већини бунара се, у мањој или већој мери, одвијало пропадање дренова услед корозије филтерских цеви и биохемијског колмирања дренова. Производња потребних количина пијаћих вода се и даље обезбеђује значајним снижењем нивоа воде у шахтовима (тј. све интензивнијим режимом експлоатације), што подразумева услове који доприносе даљој деградацији и искључењу дренова из експлоатације.

У протеклој деценији, смањење експлоатације подземних вода је имало константан тренд од око 100 l/s годишње, упркос мерама регенерације. Тренутно стање је такво да је просечан капацитет бунара са хоризонталним дреновима око 30 l/s, док је укупна експлоатација преко 96 активних бунара свега око 3  $m^3/s$  (на нивоу на ком је била пре 45 година).

Овакво стање објеката и експлоатације подземних вода указује да је неопходно приступити систематској санацији бунара на београдском изворишту, којом би већ сада била обухваћена готово половина од укупног броја изграђених бунара. Адекватан избор и рангирање бунара који су кандидати за санацију представља најважнији услов за успешно решавање питања стања водозахватних објеката на изворишту и обезбеђења стабилног водоснабдевања Београда.

Без обзира на актуелни капацитет бунара, експлоатација се манифестује формирањем одређеног динамичког нивоа подземних вода у зони утицаја. Површина нивоа подземних вода у зони бунара са хоризонталним дреновима има по правилу карактеристичан тродимензионалан изглед. Из разлога актуелног броја и стања дренова, као и хетерогеног литолошког састава и филтрационих одлика седимената водоносне средине, нивои издани у окружењу бунара београдског изворишта имају изразито просторно неправилне површине.

Управо је режим нивоа издани у непосредној зони бунара индикативан показатељ потенцијала водоносне средине у погледу расположивих количина подземних вода. Анализа режима нивоа уједно представља претходни корак у упознавању функционалног стања дренова, преко дефинисања коефицијента њихове пропусности.

Дефинисањем вредности коефицијента пропусности се може сагледати ефикасност дренова, односно утврдити у којој мери су они хидраулички функционални (чиме омогућавају експлоатацију подземних вода) или затворени процесом колмирања, неадекватним извођењем радова на утискивању и разради дренова, карактеристикама филтерских цеви и засипа (чиме је активно спречавају). Евидентно је да се у случају дефинисања хидрауличких карактеристика дренова заправо ради о дефинисању хидрогеолошке функције прифилтерске зоне, односно мере у којој она представља баријеру инфилтрацији подземних вода из издани у дренове.

У случају да непосредно уз дрен постоји изграђен адекватан осматрачки објекат, вредност овог хидрауличког параметра се може одредити према изразу који се користи за симулацију граничног услова "дрен" у савременој хидродинамичкој анализи, тј. математичком моделирању кретања подземних вода под утицајем бунара са хоризонталним дреновима. Израз је заснован на Дарсијевом закону, према ком интензитет размене подземних вода између водоносне средине и дрена (одређене дужине и пречника), за разлику у пијезометарским нивоима унутар дрена и непосредно са његове спољашње стране представља функцију водопропусности прифилтерске зоне.

Квантификацијом и поређењем вредности коефицијента пропусности дренова за различите временске пресеке, може се пратити напредовање процеса колмирања на неком бунару, што представља основу за изношење прогноза у погледу даљег пада капацитета или процене услова када ће на бунару бити потребно применити мере одржавања, односно регенерације дренова. Додатно, дефинисање вредности овог параметра пре и после спроведене регенерације, може служити као квантитативан показатељ реалне оцене њених ефеката.

Резултати спроведених прорачуна указују да гранична вредност пропусности прифилтерске зоне хоризонталног бунара предложена од стране аутора Ракк & ZHAN (2002) од  $[K_{prif}/d]=1,0\times10^{-4}$  s<sup>-1</sup>, показује добру сагласност са коефицијентом колмираности дренова у случају анализираних бунара београдског изворишта, због чега се као таква може прихватити.

У условима када прифилтерска зона има коефицијент пропусности мањи од наведене вредности (примери бунара РБ-7м и РБ-42), ефекти колмирања су сасвим евидентни. Када прифилтерска зона има повољнија филтрациона својства од декларисане вредности (примери бунара РБ-46 и РБ-8м), њени ефекти на рад бунара и експлоатацију подземних вода су практично занемарљиви. У том случају се коефицијент филтрације водоносне средине (литостратиграфског слоја у ком су утиснути дренови) начелно може сматрати еквивалентним са вредношћу коефицијента филтрације прифилтерске зоне.

Проверу добијених вредности и даљу анализу хидрауличке ефикасности дренова треба вршити у фази пројектовања оптималног решења санације дренова на одабраним бунарима. Она треба бити реализована израдом детаљног хидродинамичког модела. На овај начин биће верификована или додатно калибрисана почетна вредност коефицијента филтрације прифилтерске зоне, претходно оријентационо одређена представљеним изразом за дефинисање хидрауличких карактеристика дренова.

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# Characteristic groundwater level regimes in the capture zones of radial collector wells and importance of identification (case study of Belgrade Groundwater Source)

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Abstract. Assessment of the operating modes of radial collector wells reveals that the pumping levels in the well caissons are very low relative to the depth/elevation of the laterals, which is a common occurrence at Belgrade Groundwater Source. As a result, well discharge capacities vary over a broad range and groundwater levels in the capture zones differ even when the rate of discharge is the same. Five characteristic groundwater level regimes are identified and their origin is analyzed using representative wells as examples. The scope and type of background information needed to identify the groundwater level regime are presented and an interpretation approach is proposed for preliminary assessment of the aquifer potential at the well site for providing the needed amount of groundwater.

Key words: water supply, radial collector well, groundwater level regime.

Апстракт. Приликом анализирања режима рада бунара са хоризонталним дреновима, уочена је појава која представља готово константу на београдском изворишту подземних вода, а то је да се нивои у бунарским шахтовима налазе веома ниско у односу на дубину/коту утиснутих дренова. Као резултат оваквог стања, капацитети бунара варирају у широком дијапазону, а у непосредном окружењу бунара се формирају веома различити нивои подземних вода, чак и при истом капацитету бунара. Издвојено је пет карактеристичних режима нивоа издани, док су услови њиховог формирања анализирани на примерима репрезентативних бунара. Представљени су обим и врсте подлога којима је потребно располагати у циљу идентификације режима и предложен је приступ његовог тумачења путем ког је могуће прелиминарно дефинисати потенцијал водоносне средине на локацији бунара за обезбеђење потребних количина подземних вода.

Кључне речи: водоснабдевање, бунар са хоризонталним дреновима, режим нивоа подземних вода.

# Introduction

Operation of radial collector wells is managed by regulating water levels in the well caisson (i.e. controlling well drawdown). At Belgrade Groundwater Source (BGWS), groundwater levels in the caissons (pumping levels) have for years been low relative to the well laterals. This is primarily a result of a reduced capture capacity of the laterals, caused by multiple decades of exposure to corrosion and colmation (DIMKIĆ *et al.* 2011a, 2011b, 2012; POLOMČIĆ 2000). It is safe to say that a large drawdown and modest well discharge capacity are recognizable BGWS features today, as clear indicators of the condition of the wells and the groundwater extraction regime.

The starting point of the research reported in this paper was the observation that maintenance of, as a rule, low pumping levels in the caissons of radial collector wells has resulted in a broad range of discharge capacities (from 3 to 150 l/s), and that as a result of such an operating mode, different groundwater level regimes are formed in the zones of influence of the wells.

It is clear that the discharge capacity of a radial collector well is a function of the number and condition of active laterals, as well as the hydrologic features of

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the site and aquifer recharge conditions. As such, significant variations in the rates of groundwater extraction between the wells are indicative of large differences in the functional condition of their groundwater capture components and a pronounced heterogeneity of the lithologic composition and filtration characteristics of the porous medium in the near-well region.

Several characteristic groundwater level regimes can be identified with regard to the currently intensive operating mode (large well drawdown), such that the wells are grouped accordingly. as well as specific paleoclimate conditions throughout the Quaternary period.

Tectonic activity is manifested by multiple uplifting of the horst of Mt. Fruška Gora to the northwest and the Belgrade hills to the south, along with sinking of the Sava paleo trench between these two formations (TOLJIĆ *et al.* 2014). Dramatic global climate change during the Pleistocene is another major initiator of the origin of the characteristic polycyclic framework of the BGWS sediments. This groundwater source corroborates the rule that regional changes in the geolog-



Fig. 1. Geographic location of Belgrade Groundwater Source.

# Geologic framework and hydrogeologic features

Belgrade Groundwater Source (BGWS) is located along the Sava River, in Quaternary fluvial sediments. The boundary of the groundwater source (protection zones) encompasses, for the most part, the areal extent of the contemporary alluvial plain of the Sava River at Belgrade. Its main natural feature is an extremely heterogeneous lithostratigraphic composition and diverse hydrogeologic properties of the sediments (even in a very small space – within the capture zone of the laterals of a single radial collector well). This state of affairs is a result of a highly complex origin, based on current knowledge, associated with intensive tectonic activity in the Late Pliocene and Lower Pleistocene, ic framework are a result of tectonic activity, whereas local changes are under the influence of climate.

The impermeable aquifer floor formed in fluvial sediments is represented by so-called lacustrine-bog deposits of the Plio-Pleistocene (there are only local older rocks), composed of clay, sand and silty clay. Their thickness at BGWS has not been determined reliably, but it is believed to be greater than 100 m.

The unconfined aquifer is formed in sediments whose thickness is from 25 to 30 m in the downstream sector of the BGWS and about 20 m upstream from the Ostružnica Bridge. They are comprised of two Quaternary stratigraphic units:

- Lower Pleistocene polycyclic fluvial sediments, and
- Holocene sediments of the contemporary channels of the Sava River and its tributaries.

At BGWS, groundwater is tapped from the older Quaternary strata (previously known as the "Makiš layers" or "layers with *Corbicula fluminalis*" and today as "layers with Pleistocene *Corbicula*" – GAUDÉ-NYI *et al.* 2015). The structure of both old and recent water-bearing sediments is polycyclic, as a result of multiple sedimentation stages of bed-load deposits and floodplain deposits, with frequent formations of oxbow lake deposits.

Common to all cycles is that, as a rule, there are strata of bed-load deposits, comprised of gravel and sand, towards the bottom, which turn sandy near the bed surface and feature different grain sizes.

The final part of each cycle consists of local sediments of floodplain deposits: clay, silty clay and silt. With regard to groundwater extraction and operation of the radial collector wells, the hydrogeologic significance of these ultimate stages of the sedimentation cycles (which are generally referred to as a "semi-permeable interbed") is exceptional. Given that they are semi-permeable rocks, they constitute a barrier for groundwater flow to the laterals. As such, their presence limits and impedes groundwater extraction and operation of the wells.

In the contemporary Sava Valley, Holocene sediments lie discordantly over Lower Pleistocene strata. Middle and Upper Pleistocene fine-grain sediments had previously been severely eroded in the Holocene river channel stage. The average thickness of these strata is 10–15 m.

On the ground surface, there are recent floodplain sediments, which virtually cover the entire alluvial plain of the Sava River. They are comprised of silt, silty sand, and silty and fine sandy clay. They provide sound protection of the aquifer against pollution from the ground surface.

The highly–complex framework of the BGWS fluvial deposits is currently explained most fully by Shantser's model of the constrative dynamic phase of alluvium formation (NENADIĆ *et al.* 2010), along with the influence of tributaries from the slopes that form the perimeter of the alluvial plain (KNEŽEVIĆ *et al.* 2012). However, sudden lateral alternation of sediments featuring different lithologic and geochemical compositions, often only a few meters apart, indicates that this model is simplified but still effectively used to address practical engineering problems (where it is, as a rule, enough to define the vertical lithologic stratification).

Additional exploration is needed to identify the effect of the tributaries on aggradation of the Sava trench in the Pleistocene. Given the past individual efforts and the contributions of those who explored this terrain, a team of explorers from different geological disciplines (along with required resources) is needed to develop a proper geological model of the origin of the BGWS terrain.

# **Characteristic groundwater level regimes**

**Regime 1**: This characteristic groundwater level regime is found in conditions where the pumping level is at a small height above the laterals, which results in a significant drawdown in the capture zone of the laterals, distinct spatial irregularity of the groundwater levels in the zone of influence of groundwater extraction, and modest well discharge capacity.

A typical example of this groundwater level regime is well RB-46. Over the past five years, the pumping level has been maintained at 55.40 m above sea level (3 m above the laterals), which has resulted in a discharge rate of some 20 l/s (Fig. 2).



Fig. 2. Discharge capacity of well RB-46.

(Explanation: IJČ and BVK denote monitoring campaigns undertaken by Jaroslav Černi Institute for the Development of Water Resources and Belgrade Waterworks and Sewerage PUC, respectively; P stands for a spring campaign and J for an autumn campaign.)

The condition of the laterals of well RB-46 is poor. Underwater filming of the inside of the laterals revealed that five of the six active laterals were significantly filled with aquifer material at the very inlet (solid pipe).

Since the actual lengths of the laterals could not be determined accurately, all the active laterals were simulated on the hydrodynamic model (Božović *et al.* 2015) as having a screen length of 20 m. Detailed calibration of the hydrodynamic model, which simulated perennial groundwater regime, revealed that only three laterals were actively involved in groundwater extraction.

There are three observation wells (RB-46/P-1, P-2 and P-3) in the capture zone of well RB-46, whose piezometer screens are short and installed at the same depth as the laterals (an important condition in studies of groundwater level regimes in the zone of influence of radial collector wells). The groundwater level differences (Fig. 3) reported by these piezometers are substantial, which leads to the conclusion that they are distinctly a function of distance from the functional 46

laterals. Immediately beyond the capture zone of the laterals, the groundwater levels are not influenced by the well. Instead, they fluctuate according to river stage variation. VIĆ *et al.* 2015). The considerable aquifer drawdown (up to 10 m) in the capture zone of the laterals suggests that the filtration properties of the other lithostratigraphic layers (not only those of the layer in



Fig. 3. Groundwater levels in the zone of influence of well RB-46.



Fig. 4. Water table in the zone of influence of well RB-46 (on 25 Oct. 2012, Božović *et al.* 2015).

This groundwater level regime is determined by modest filtration characteristics of the aquifer in the area of the well. Specifically, the hydraulic conductivity of the layer in which the laterals of well RB-46 are emplaced is  $K=1\cdot10^{-4}$  m/s. There is not much of the semi-permeable interbed in this zone. The small difference between the pumping level and the groundwater level at piezometer RB-46/P-1, which is located adjacent to (or in technical jargon "on") lateral No. 8, indicates that this lateral is not significantly colmated. This has been corroborated by model testing (Božowhich the laterals are emplaced) are modest. As such, the wells in this group cannot be expected to provide substantial amounts of water. This was corroborated by hydrodynamic analysis, which examined the effectiveness of replacing the old laterals of this well by installing six new, 50 m long laterals. Model simulations showed that the discharge capacity of only 35 l/s was to be anticipated (when the stages of the Sava River are low and when the pumping level is 6 m above the elevation of the laterals, according to Božović et al. 2016a).

It follows that in this characteristic groundwater level regime, when the pumping level is low, there is a significant aquifer drawdown adjacent to the lateral. As the distance from the lateral increases (even at the center distance between two neighboring laterals), the groundwater level increases progressively and the water table acquires a characteristic three-dimensional pattern (Fig. 4). The discharge capacities of this group of wells are modest even when the laterals are in good condition.

**Regime 2**: In this group of wells, when the pumping level is low, the groundwater level in the zone of influence of the well remains high above the laterals (close to the ground surface), which results in a modest well discharge capacity. The reason for this is colmation of the laterals, which reduces the porosity of the screen and filtration characteristics of the skin zone and thus hinders groundwater infiltration into the laterals and prevents a higher discharge capacity of the laterals and the well itself.

Well RB-7m was selected to portray the groundwater extraction and flow conditions typical of this regime. The condition of the laterals of well RB-7m is rather poor. Out of the eight laterals installed in 1978, over the past 20 years only four have remained open but they are so filled with aquifer material that they could not be filmed over a distance of more than a few meters (Fig. 5).

The presence of boulders and fragments of the aquifer matrix inside the laterals indicates that the screens are severely damaged (by corrosion) and that mechanical rehabilitation is no longer a viable option. Since it will not be possible to increase the discharge capacity of this well while retaining the old laterals, emplacement of new laterals is required.



Fig. 5. Lateral filled with aquifer material.

The laterals of this well are installed at an elevation of 51.50 m.a.s.l. and the pumping level is maintained at about 56.50 m.a.s.l. The well discharge capacity has for years been roughly 20 l/s (Fig. 6).



Fig. 6. Discharge capacity of well RB-7m.



Fig. 7. Groundwater levels in the zone of influence of well RB-7m.

Groundwater levels in the zone of influence of well RB-7m, which is monitored by means of three new piezometers, are under the dominant influence of river stage variations, or rather changes in water levels of a nearby channel which is in hydraulic contact with the river. The drawdown caused by pumping has been tested on several occasions by multiple-day recovery tests and restarting of the well. The findings were that the aquifer drawdown was virtually negligible relative to the quasi-static groundwater level of the aquifer and that it did not exceed 1 m at the piezometers, while the caisson drawdown was 12–15 m (Technical report).

In general, the groundwater levels in the area of well RB-7m fluctuated between 67 and 70 m.a.s.l. (Fig. 7). At medium and low stages of the Sava River, the difference between the groundwater level and the river stage was about 3 m. It decreased with increasing stages, such that at high stages (above 73 m.a.s.l.), the groundwater level was close to the ground surface, despite pumping.

The fact that at 20 l/s there is a practically negligible aquifer drawdown (contrary to that of well RB-46, which is 10 m at the piezometer closest to a lateral and which registered the lowest levels, at the same pumping rate and similar states of the laterals), indicates that the capacity of the site of well RB-7m is considerable. This was corroborated by hydrodynamic analysis, which showed that installation of five new laterals at the same depth as the existing laterals, with a pumping level of 6 m above the laterals, will result in a discharge of 75 l/s (Božović *et al.* 2016a).

Given that the laterals of this well, like on most BGWS wells, are not installed in the layer that features the best grain-size distribution and filtration characteristics (as a rule, this is the lowest/oldest layer), hydrodynamic modeling was undertaken to test the emplacement of new laterals in that layer, which requires prior reconstruction of the caisson (according

to Božović *et al.* 2016b, 2016c). The results suggest that in such a case the achievable rate of groundwater extraction is close to 100 l/s (Božović *et al.* 2016a).

**Regime 3**: In this case, maintenance of a low pumping level results in a high discharge capacity of the well. A high rate of groundwater extraction at any site is coupled with a considerable drawdown and is achievable only if the functional condition of the laterals is good, if there are many laterals, if they are long enough and if the hydrogeological conditions are favorable. A high discharge capacity of the laterals means that they are hydraulically open (i.e. not colmated), such that the differences between the pumping level and the groundwater level of the aquifer in the capture zone of the laterals are small.

Well RB-23 is an example of this type of groundwater flow and extraction. The well features the highest discharge rate at BGWS. In 2015, the pumping level was maintained at 54.0 m.a.s.l. and the resulting discharge rate was 150 l/s (Fig. 8).



Fig. 8. Discharge capacity of well RB-23.

Neighboring wells RB-22 and RB-21, located upstream and downstream from representative well RB-23 (Fig. 9), are also high–capacity wells. In general, this part of BGWS is a zone of a superior mechanical composition, filtration characteristics of the sediments and hydrochemical quality of the groundwater, where average well discharges are higher than in other parts of BGWS (DIMKIĆ *et al.* 2011a). A decline in capacity of a single well (usually due to pumping level increase) boosts the discharge capacity of the neighboring well, leaving the impression of a "well–developed" water-bearing medium.

The laterals of well RB-23 have been emplaced at two elevations. There are eight laterals at 47.80 m.a.s.l. and six at 56.30 m.a.s.l. The lower laterals were filmed by an underwater camera and their length found to be 384 m. It was interesting to note that the laterals were vertically displaced, but pointing downward (to the aquifer floor), which is a rare occurrence given that displacements tend to be in the upward direction. Although the caisson openings are at 47.80 m.a.s.l., the laterals are emplaced at depths ranging from 47.80 to 44.00 m.a.s.l. As a result of displacement, the laterals tap the layer that features the best filtration characteristics (first Pleistocene sedimentation cycle), which has had a favorable impact on the discharge capacity of the well. It is evident that such a capacity of well RB-23 would not have been achieved, even if the condition of the laterals was good, had not the aquifer potential at this location been very high.

The groundwater surface in the capture zone of well RB-23 is typical of a high hydraulic conductivi-

ty aquifer: the impact of groundwater extraction spreads far beyond the capture zone of the laterals and the groundwater surface in this zone features a low groundwater level gradient. However, the groundwater levels in the capture zone of this well are low relative to the pumping level, meaning that the groundwater level is not really consistent with that expected in a setting where hydraulic conductivity is high, even with such a substantial well discharge capacity. The actual situation therefore suggests that there is something that causes additional drawdown in the extended area of the well, which requires a more detailed study for a full understanding of the regime.

Exploratory boring revealed the presence of the interbed, lithologically represented by 3 m thick silty clay, whose spread in this part of BGWS is considerable (and the reason for two levels of laterals). The hydraulic role of the interbed is such that it virtually divides the aquifer into two parts – shallow and deep. As a result, observation wells are paired. A pair is comprised of a piezometer whose screen is in the lower part of the aquifer and a piezometer in the shallow part (below and above the interbed).

The Sava River has incised its channel shallow in the capture zone of well RB-23 (up to an elevation of 64 m.a.s.l.). The interbed also spreads below the riverbed, corroborated by observation wells drilled from the river surface. The interbed causes active infiltration of surface water only into the shallow part of the aquifer and thus the groundwater levels recorded by the "shallow" piezometers respond more strongly to river stage variation than the "deep" piezometers. The groundwater levels at the deep piezometers are predominantly affected by pumping, such that their response to river stage fluctuations is not as pronounced. The average groundwater level at the shallow piezometers, RB-23/P-2 and RB-23/P-4, over the past ten years has been at 59.94 and 60.78 m.a.s.l., respectively. At the same time, the groundwater level recorded by the deep piezometers (RB-23/P-1 and RB-23/P-3) has been at 57.12 and 58.47 m.a.s.l., respectively. As such, the difference between groundwater levels recorded by the deep and shallow piezometers is about  $\Delta h=2.5$  m and they are only one meter apart.

The plot of groundwater level fluctuation at the piezometers (Fig. 10) also corroborates a considerable spread of the interbed. The lowest groundwater level is registered by piezometer RB-23/P-1, which is located "on" lateral No. 1. The difference between this groundwater level and the pumping level is minimal, which is an indication that the lateral is hydraulically open and in good condition. Over the past three years, the difference between the groundwater levels at RB-23/P-1 and the shallow piezometer with which it is paired has been about 4.5 m and is the highest among the piezometer pairs, as expected. This difference is 3.5 m in the case of observation wells RB-23/P-2 and P-4, which are located within the capture zone of the



Fig. 9. Locations of observation wells in the zone of influence of production well RB–23.



Fig. 10. Groundwater levels in the zone of influence of well RB–23.

laterals but farther away from the well caisson. However, the differences in groundwater levels between the shallow and deep piezometers of pairs ZNB-1 and ZNB-2 are large (about 2 m), even though they are at a significant distance from the caisson of well RB-23 (150 m and 200 m, Fig. 9). This is attributable to the presence of the semi-permeable interbed, which causes the effect of pumping to be transmitted far from the immediate zone of the well. If that were not the case, the groundwater levels at these observation wells would have been equal.

**Regime 4**: In this regime, the pumping levels are low, the well discharge capacity is sound (higher than the present BGWS average) and the drawdown in the capture zone of the laterals is moderate. The wells in this group feature groundwater levels between those of the first and second characteristic regimes. Well RB-41 is an example.

Over the past five years, the discharge capacity of well RB-41 has been 40–45 l/s (Fig. 11). The pump-

ing levels have been maintained at 51.75 m.a.s.l., on average. The laterals are located at 48.25 m.a.s.l., meaning that the pumping level in the well caisson is rather low and only 3.5 m above the laterals.

Compared to the initial state, the current condition of the laterals is such that they are only partly functional. Out of the eight installed laterals, only six are open at present, of which four have retained most of their initial lengths (from 43 to 54 m). The lengths of the remaining two, according to a video recording, are 15 and 20 m. The inside of the laterals was filmed in 2007, showing that corrosion of the screen pipes has caused many of the slots to become enlarged or groups of slots to be joined together. As a result, there is coarse material from the porous medium inside the laterals. Only one lateral exhibits a significant vertical displacement.

In the vicinity of this well there are three old piezometers with 1.5 m long screens at a depth of about 20 m. There are also five new piezometers, two of which form a pair. The screen length of the new deep piezometers is 3 m, generally in the depth range of 24.5–27.5 m.

Semi-permeable sediments have been detected only locally, in the zone of piezometer RB-41/P-1.



Fig. 11. Discharge capacity of well RB-41.

The groundwater levels recorded at the observation wells fluctuate over a broad range, 60–70 m.a.s.l.

(Fig. 12). The groundwater level at the piezometers is a function of their distance from the laterals, which are rather long. At the same time, all the piezometers respond quite strongly to river stage variation.



Fig. 12. Groundwater levels in the zone of influence of well RB-41

Piezometer RB-41/P-1 registers the lowest groundwater levels. Since it was installed in 2008, the groundwater levels at this location have been in the interval 59.5–63.5 m.a.s.l. However, over the past three years the groundwater levels at this piezometer have been somewhat higher, with a mild upward trend. It has been at 62.80 m.a.s.l., on average, and the river stage participation during that period was about 50% (71.20 m.a.s.l.). As such, river stages did not cause the groundwater levels in the well capture zone to rise. Instead, this state of affairs is indicative of colmation/deterioration of the laterals due to high pumping rates and wear–and–tear.

The aquifer drawdown in the zone of influence of the wells of this group is not very pronounced, which indicates that the filtration characteristics of the aquifer are sound. Additionally, it shows that the groundwater levels are affected by both pumping and river stage fluctuations, given that the river is the main source of aquifer recharge. For this reason it is realistic to expect that replacement of laterals in this group of wells will result in a significant capacity increase (of course, when discharge rates fall to or below the current average).

**Regime 5**: The last of the characteristic groundwater level regimes pertains to wells whose laterals are exposed to pronounced colmation. Well ageing is a process that leads to a decline in discharge capacity for various reasons (natural, anthropogenic and their synergy). Colmation is one of the specific forms of well ageing, typical of radial collector wells at BGWS. Namely, BGWS wells are often colmated by iron sedimentation (iron concentrations in the groundwater are high, 2–4 mg/l according to DIMKIĆ *et al.* (2011a), although not evenly distributed over space), due to specific geochemical, hydrochemical, microbiological, lithologic and grain-size conditions of the geological setting and the groundwater, as well as by products of bacterial activity.

> As a rule, a decline in well discharge capacity due to biochemical or mechanical colmation is manifested differently from that caused by corrosion. Corrosion leads to degradation of the material from which the screen pipes are made, such that their physical characteristics are altered. Corrosion is initially accompanied by gradual filling of the pipe with aquifer material and once structural integrity is lost, a part of or the entire lateral collapses. This affects the operating mode of the well (i.e. the pumping level) and the rate of discharge declines

as a result. In essence, corrosion of screen pipes and colmation of laterals have different causes and manifestations, but the final outcome is the same (PO-LOMČIĆ, 2001).

In cases where it is not possible to make a video recording of the inside of the laterals, the effect of the collapse or colmation of a lateral can be identified by analyzing well discharge variations and groundwater level fluctuations in the capture zone. Given that a total or partial collapse of a lateral is nearly instantaneous, the well discharge capacity changes/declines suddenly. Conversely, colmation is a rather slow process and the decline in discharge capacity generally exhibits a uniform trend.

Well RB-42 is a representative example of the group of wells where the decline in capacity is caused by colmation of laterals. The concentration of bivalent iron in this well is about 2.5 mg/l and that of total iron greater than 3.0 mg/l. All the laterals of the well are open, but five are filled at the very beginning. Three laterals (nos. 1, 7 and 8) have retained their original lengths. The laterals are emplaced at an elevation of 50.50 m.a.s.l. The pumping level has for many years been maintained at 53.50 m.a.s.l., and then began to fluctuate around 55.25 m.a.s.l. three years ago. Over the past decade, the discharge capacity declined from more than 50 l/s to less than 10 l/s (Fig. 13), even though the pumping levels had not changed by much.

There are two piezometers (Prb-42-1 and Prb-42-2) in the capture zone of the laterals and one (Prb-42-z) beyond. When installed, they revealed the presence of the interbed, which explains the large difference in groundwater levels between the capture zone of the laterals and the area beyond (especially at the beginning of the analyzed time period, Fig. 14).



Fig. 13. Discharge capacity of well RB-42.



Fig. 14. Groundwater levels in the zone of influence of well RB-42.

The BGWS management practice is such that when a decrease in well discharge is noted, an attempt is made, as a rule, to compensate by lowering the pumping level in the caisson. Given that the pumping level in well RB-42 has been lowered as far as possible, it is not possible to increase the discharge rate on account of additional drawdown. Mechanical rehabilitation of the laterals would certainly result in damage and collapse of three functional laterals. Consequently, the discharge capacity of this well can only be increased by installing new laterals. A further decline in discharge capacity, and the resulting increase in groundwater levels in the capture zone of this well, can be predicted from Figs. 12 and 13. A total loss of the capture capability of the laterals would equate the groundwater levels at piezometers Prb-42-1 and Prb-42-2 in the capture zone of the laterals with that of piezometer Prb-42-z, which is farther inland.

In the case of wells that exhibit clear signs of colmation, at low pumping levels the discharge capacity gradually declines over time. This decline is manifested by groundwater level variation in the capture zone of the laterals, which rises slowly but continually.

In a certain number of wells in this group, colmation can be slowed down by rehabilitation, although such wells have been fewer from year to year and the effects of rehabilitation less and less notable.

# Conclusions

Today, the functional state of radial well laterals has a dominant effect on the well discharge capacity at Belgrade Groundwater Source. The condition of screen pipes and the hydraulic characteristics of the skin zone are the main reasons for the significant decline in pumping levels in the well caissons and modest discharge capacities of the wells.

> The present research has shown that assessment of the effect of operation of radial collector wells on groundwater levels in their immediate vicinity needs to be founded upon recognition of the characteristic spatial heterogeneity of the lithologic composition and filtration characteristic of the aquifer layer tapped by this type of wells (usually of Quaternary age and alluvial origin).

> In order to analyze the groundwater level regime in the capture zones of radial collector wells, certain information is needed about the condition of the functional laterals,

pumping levels, groundwater level fluctuations at suitably designed and located observation wells, and the main indicators of the biochemical composition of the groundwater.

Identification and analysis of the groundwater level regime in the capture zone of a radial collector well constitute a reliable, representative and relatively simple method for gaining insight into the well site potential in terms of groundwater withdrawal and creating conditions for proper selection of wells that need to be rehabilitated or their degraded and non-functional old laterals replaced.

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# Резиме

# Карактеристични режими нивоа издани у зони бунара са хоризонталним дреновима и значај њихове идентификације (примери београдског изворишта подземних вода)

Управљање режимом рада бунара са хоризонталним дреновима врши се контролисаним снижењем нивоа воде у водосабирном бунарском шахту. Оборени радни нивои, заједно са скромним просечним капацитетом бунара данас представљају препознатљиву одлику београдског изворишта подземних вода и јасан показатељ стања водозахватних објеката и режима експлоатације подземних вода на њему.

Уочено је да одржавање ниских нивоа подземних вода у бунарима има за резултат капацитете чије се вредности крећу у широком дијапазону, од 3 до 150 l/s, као и да се у непосредној зони утицаја бунара/експлоатације подземних вода формирају веома различити режими нивоа издани. Капацитети бунара су свакако функција броја и стања активних дренова, као и хидрогеолошких одлика и услова прихрањивања водоносне средине. Стога, велике разлике у количини захваћених подземних вода између бунара указују на велике разлике у функционалном стању њихових водопријемних делова, као и на изражену хетерогеност литолошког састава и филтрационих карактеристика средине у непосредном окружењу бунара.

Управо се за просторну хетерогеност литостратиграфског састава седимената (чак и на сасвим малом простору – у зони лепезе дренова једног бунара) може рећи да представља основну природну одлику београдског изворишта подземних вода. Овакво стање је резултат комплексних услова генезе, према актуелним схватањима везане за интензивну тектонску активност која се одвијала током краја плиоцена и доњег плеистоцена, као и за специфичне палеоклиматске услове током целог плеистоцена.

У односу на постојећи интензиван режим рада бунара, може се препознати и издвојити неколико карактеристичних режима нивоа подземних вода, због чега се и бунари могу сврстати у више група.

Први издвојени режим нивоа подземних вода је присутан код оних бунара код којих се ниво воде у бунарском шахту налази на малој висини изнад дренова, што за резултат има значајно снижење нивоа подземних вода у издани у зони лепезе дренова, изразито просторно неправилне нивое у зони утицаја експлоатације и скроман капацитет бунара. Разлог за настанак оваквог нивоа издани су скромне филтрационе карактеристике водоносне средине у непосредном окружењу бунара. Ова чињеница указује да се обављањем дренова на бунарима који припадају овој групи не може очекивати захватање значајнијих количина подземних вода.

Код групе бунара који припадају другом издвојеном режиму нивоа издани, при обореном нивоу воде у шахту, ниво подземних вода у зони бунара остаје плитко испод површине терена, односно високо изнад нивоа у шахту, што резултира скромним капацитетом бунара. Разлог оваквог стања је процес колмирања дренова који доводи до смањења порозности филтерске конструкције и прифилтерске зоне, чиме спречава инфилтрацију воде у дренове и остваривање већег капацитета дренова, а самим тим и бунара. У случају када су дренови на бунарима ове групе у лошем функционалном стању (са крупним оштећењима на филтерској конструкцији, зарушени делом почетне дужине, запуњени материјалом порозне средине), механичке регенерације више није оправдано изводити, због чега се капацитет бунара може повратити само утискивањем нових дренова.

Трећој групи припадају они бунари код којих одржавање ниског нивоа воде у шахту има за резултат висок капацитет бунара. Експлоатација значајних количина подземних вода на било којој локацији на београдском изворишту условљава и значајно снижење нивоа издани. Могуће ју је остварити само у случају доброг функционалног стања, већег броја и дужине дренова, уз повољније хидрогеолошке услове. Висок капацитет дренова значи да су они хидраулички отворени, тј. да нису колмирани, због чега је разлика између нивоа воде у бунарском шахту и нивоа у издани у зони лепезе дренова мала.

Четврти карактеристичан режим нивоа подземних вода је везан за оне бунаре код којих се у условима ниских радних нивоа остварују солидни капацитети бунара (изнад данашњег просека), док је снижење нивоа у зони дренова умерено, односно није значајније изражено. Као такво, оно указује на солидне филтрационе карактеристике водоносне средине. Поред тога, оно указује да се нивои осим под утицајем рада бунара налазе и под утицајем промене водостаја реке као главног извора прихрањивања издани. Из тог разлога се санацијом дренова на бунарима који припадају овој групи у односу на карактеристични режим нивоа, може очекивати остваривање значајнијих капацитета.

Последњи од анализираних режима нивоа издани је присутан код оних бунара на којима је констатован процес колмирања дренова. За разлику од бунара другог карактеристичног режима, овде је он још увек у активној фази. У случају бунара на којима су евидентни ефекти процеса колмирања, при ниском нивоу воде у шахту током времена експлоатације долази до постепеног смањења капацитета бунара. Смањење капацитета се манифестује континуираним променама нивоа подземних вода у зони дренова, тако што ниво издани благо и константно расте.

Услед специфичних геохемијских и литолошких услова геолошке средине и хемијског и микробиолошког састава подземних вода, на бунарима београдског изворишта је често заступљено колмирање изазвано таложењем гвожђа (чији је садржај у подземним водама изворишта висок, мада просторно неравномеран) и продуката активности одређених врста бактерија. Опадање капацитета бунара услед биохемијског или механичког колмирања дренова се по правилу различито манифестује од опадања капацитета које се дешава услед корозије.

Ефекти колмирања се могу идентификовати анализом промене капацитета бунара и осцилација нивоа подземних вода у његовој непосредној зони. Како се зарушавање дела дрена услед корозије филтерских цеви дешава готово тренутно, то се и капацитет бунара нагло мења, односно смањује. Колмирање се, са друге стране, одвија релативно споро, због чега опадање капацитета има генерално равномеран тренд.

На одређеном броју бунара који припадају овој групи, процес колмирања се може успорити спровођењем регенерације, мада је објективно број таквих објеката из године у годину све мањи, а ефекти спроведених мера све дискретнији.

У циљу анализе режима нивоа издани у зони бунара са хоризонталним дреновима, потребно је располагати одређеним информацијама о: стању активних дренова, нивоима вода у шахтовима бунара, осцилацијама нивоа подземних вода у осматрачким објектима адекватне конструкције и позиције у односу на дренове, основним показатељима хемијског и микробиолошког састава захваћених подземних вода.

Спроведено истраживање је указало да анализа ефеката рада бунара са хоризонталним дреновима у смислу формираних нивоа издани у њиховом непосредном окружењу треба бити утемељена на перманентном уважавању карактеристичне просторне хетерогености литолошког састава и филтрационих карактеристика седимената водоносне средине у којима се ови објекти изводе.

Идентификација и анализа режима нивоа подземних вода у зони бунара са хоризонталним дреновима представља репрезентативан и релативно једноставан механизам којим се, на нивоу претходог сагледавања, могу дефинисати потенцијал локације бунара у погледу расположивих количина подземних вода и услови за правилан избор објеката које је потребно санирати, тј. извршити замену дотрајалих и нефункционалних старих дренова адекватним новим дреновима.

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# Geological activity of humans represented in the World Heritage Sites of India, Italy, and Russia: Evidence of the Anthropocene

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**Abstract.** The idea of the Anthropocene attracts attention of scientists, policy-makers, and broad public to the geological activity of humans and poses new important questions for the modern stratigraphy. The growth of the Anthropocene-related knowledge and its promotion can be based potentially on the UNESCO World Heritage Sites (WHS). On the one hand, many of these sites provide spectacular evidence of the human activity. On the other hand, these are remarkable tourist attractions. The WHSs of three heritage-rich countries, namely India, Italy, and Russia, have been assessed with regard to how these reflect the geological activity of humans. It is established that 65–90% of all WHSs in each country provide direct and indirect evidence of such an activity (artificial caves, terrace building, etc.), which appears to be enough for the general discussion of the idea of the Anthropocene. However, the distribution of the WHSs by their age allows focusing only on the "early" (before 1800 AD) start of the Anthropocene, which is not enough for full discussion of the lower limit of this unit. The examples considered in the present study imply that some WHSs alone provide very important pieces of the Anthropocene-related knowledge.

Key words: Geoarchaeology, World Heritage Site, human activity, Anthropocene, India, Italy, Russia.

Апстракт. Концепт антропоцена усмерава пажњу истраживача, креатора јавне политике и шире јавности на геолошку активност човека и отвара нове значајне проблеме у оквиру модерне стратиграфије. Локалитети светске баштине под заштитом УНЕСКА (ЛСБ) могу потенцијално бити значајни за ширење сазнања о антропоцену и промовисање овог концепта. Многи од ових локалитета пружају изузетно важне доказе људске активности. С друге стране, ради се о значајним туристичким локалитетима.

Истраживани су ЛСБ на територијама три земље богате светском баштином, Индије, Италије и Русије, у циљу процене видљивих трагова геолошке активности човека на овим локалитетима. Утврђено је да 65–90% укупног броја ЛСБ у свакој од земаља пружа директне и индиректне доказе о оваквој активности (вештачке пећине, терасаст рељеф, итд.), што је изгледа довољно за генералну дискусију о концепту антропоцена.

Међутим, иако дистрибуција анализираних ЛСБ по старости иде у прилог "раном" (пре 1800. год.) почетку антропоцена, добијени подаци нису довољни за комплетнију дискусију о доњој граници овог одељка. Примери наведени у овом раду показују да неки од разматраних ЛСБ пружају изузетно значајна сазнања везана за концепт антропоцена.

**Кључне речи:** Геоархеологија, светска баштина, људска активност, антропоцен, Индија, Италија, Русија.

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# Introduction

The Anthropocene is a relatively new idea, but it has already attracted a lot of attention of researchers (CRUTZEN & SOTERMER 2000; CRUTZEN 2002; RUBAN 2008; ZALASIEWICZ et al. 2008, 2014, 2015; RUDDI-MAN 2013; BROWN 2014; JORDAN & PROSSER 2014; WATERS et al. 2014a, 2016; BEACH et al. 2015; LEWIS & MASLIN 2015; BRONDIZIO et al. 2016). Generally, this idea consists of two closely related propositions. Firstly, the Anthropocene reflects the geological (including geomorphological) activity of humans. This does not only indicate their ability to influence a geological environment, but also stresses that such an influence is of geological scale, i.e., it is more or less comparable in strength to the other geological forces (e.g., mass wasting, volcanism, wind erosion, etc.). The evidences are reported by many specialists (Ho-OKE 2000; CRUTZEN 2002; RUDDIMAN 2005, 2013; WILKINSON 2005; BROWN 2014; GOUDIE 2013; DIRZO et al. 2014; ZALASIEWICZ et al. 2015). Secondly, the Anthropocene is treated in terms of stratigraphy (for general review of this subject see WATERS et al. 2014a, 2016; HEAD & GIBBARD 2015; LEWIS & MA-SLIN 2015). It appears on the geological time scale as a new epoch or formal/informal unit of any other rank. It should be emphasized that there are different views on the duration of the Anthropocene. Some advocate its beginning since the 1800s or even later (COHEN 2014; WATERS et al. 2014b, 2016; ZALASIEWICZ et al. 2008, 2014, 2015; HEAD & GIBBARD 2015), while other suggest much earlier start, somewhere in the middle of the Holocene (cf. RUDDIMAN 2013; WA-GREICH 2014). The noted difference in views only increases the curiosity of specialists and broad public in the Anthropocene-related knowledge.

Evidently, there is an urgent requirement to find out appropriate geological objects for 1) research on the Anthropocene issues and arguing particular points of view (e.g., on its lower boundary - see JORDAN & PROSSER 2014; WATERS 2014a,b; ZALASIEWICZ et al. 2014; LEWIS & MASLIN 2015) and 2) promotion of the relevant knowledge to increase public awareness and to justify policy-making (e.g., LÖVBRAND et al. 2009, 2015; DALBY 2013; HOUSTON 2013; BRONDIZIO et al. 2016). The best evidence of the Anthropocene comes from places where geological and cultural records coexist. In fact, many cultural (archaeological and historical) sites are important for understanding the geological-scale activity of the man (e.g., MORONI et al. 2015). However, the UNESCO World Heritage Sites (WHS) are potentially of utmost importance. These are exceptional by definition, and if these are manmade features linked to the disturbance of the geological environment, they are almost ideal to study the geological-scale activity of humans and, therefore, to provide material for discussion on what is the Anthropocene and when has it started. Moreover, almost all

WHSs are important tourist attractions that are already in use (YANG *et al.* 2010; PORIA *et al.* 2013; SU & LIN 2014; WANG *et al.* 2015), thus these can be used efficiently to promote the Anthropocene-related knowledge. Similar ideas have been developed by MI-GON (2009) on the basis of the famous site of Petra in Jordan and later by GONTAREVA *et al.* (2015) on the basis of the not less famous Ajanta Caves in India. Moreover, the recent suggestions of JORDAN & PROSS-ER (2014), BEACH *et al.* (2015) and DEL LAMA *et al.* (2015) echo these ideas as well.

The main objective of the present work is to summarize the available information on the geological activity of humans represented in the WHSs of three large countries boasting by rich heritage, namely India, Italy and Russia, in order to understand their potential to provide the Anthropocene-related knowledge. In this paper, the authors do not tend to advocate the formal or informal, short-term or long-term understanding of the Anthropocene. They emphasize the evidence of geological activity of humans in the past, available from the WHSs and valuable for further debates on the essence and the time limits of the Anthropocene.

# Material

The short and long descriptions of all Indian, Italian, and Russian WHSs presented on the official webpage of the UNESCO World Heritage Centre (http://whc.unesco.org/en/list/) serve as a main material for the present study. The authors also consider their own field observations (particularly, they visited the Ajanta Caves and the Ellora Caves in India, the Cilento and Vallo di Diano National Park with the Archeological Sites of Paestum and Velia, and the Certosa di Padula in Italy, the Cultural and Historic Ensemble of the Solovetsky Islands and the Historic and Architectural Complex of the Kazan Kremlin in Russia).

# Method

The present study is realized in four steps. First, the presence of various signs of the geological activity of humans is checked for each WHS in all three countries to establish direct or indirect evidence of such activity. Direct evidence means the presence of signs that permit to visualize the kind and the strength of the anthropogenic influence on the geological environment at a particular site (Table 1). It is enough to turn attention to these signs in order to realize this influence. Indirect evidence means the presence of signs that do not indicate any geological activity of humans at a given site, but permit to judge about such an anthropogenic influence (Table 1). Adequate expla-

Evidence	Signs (selected examples)
Direct	<ul> <li>artificial caves</li> <li>construction of new landforms</li> <li>engineering geological solutions</li> <li>mines and quarries</li> <li>rock art</li> <li>rock carving</li> <li>terrace building</li> </ul>
Indirect	<ul> <li>constructions =&gt; extraction of building materials</li> <li>creating cultural landscapes =&gt; modification of natural topography</li> <li>remains/ruins of past civilizations =&gt; agricultural influences on geological environment and palaeoclimate</li> </ul>

Table 1. Signs of the geological activity of humans from the UNESCO WHSs.

nations of these signs are necessary in order to judge about this influence. For instance, some WHSs represent constructions (or ruins) made by past civilizations. It is well-known that the agricultural activity affected the global climate (e.g., via methane emission from rice paddies and perturbation of the carbon cycle as a result of forest clearance), thus humans became a geological force (RUDDIMAN 2001, 2005, 2013; LI *et al.* 2009; FULLER *et al.* 2011; ZHOU 2012). Similarly,



Fig. 1. Geographical location of the WHSs considered as examples in the present paper. Abbreviations: **AI**. Aeolian Islands; **CVD**. Cilento and Vallo di Diano National Park with the Archaeological Sites of Paestum and Velia, and the Certosa di Padula; **EC**. Ellora Caves; **KK**. Historic and Architectural Complex of the Kazan Kremlin; **SI**. Cultural and Historic Ensemble of the Solovetsky Islands.

colossal constructions built with natural stones indicate geological activity of humans because of the relevant voluminous extraction (e.g., quarrying) of building material somewhere.

Second, the time of the geological activity of humans (age) relevant to each given WHS is established on the basis of various information and, first of all, the above-mentioned official UNESCO descriptions.

Third, two analytical procedures are used. The proportion of the WHSs with direct and indirect evidence of geological activity of humans is measured for each country. The approximate distribution of these sites by their age is considered. All this led to conclusions on how significant is this evidence and how relevant is it to the idea of the Anthropocene.

Fourth, particular attention is paid to certain representative examples of the WHSs that can potentially contribute to the Anthropocene-related knowledge (Fig. 1).

# Evidence of the geological activity of humans from heritage sites

# India

Among 32 WHSs established in India, 75% bear direct and/or indirect evidence of geological activity of humans and 22% bear direct evidence (Table 2). The majority of them represent the 0–1800 AD time interval (Fig. 2). The most impressive are the WHSs with artificial caves (e.g., the Ajanta Caves), construction of which required significant intervention of humans in the geological environment (GONTAREVA *et al.* 2015). The rise of the past empires (e.g., the Great Mughals) in the history of India resulted in monumental construction that required extraction of the huge volume of building material.

WHS	Evidence of geological activity of humans
Agra Fort	Indirect
Ajanta Caves	Direct (artificial caves)
Ellora Caves	Direct (artificial caves)
Taj Mahal	Indirect
Group of Monuments at Mahabalipuram	Direct (rock art, rock carving) and indirect
Sun Temple, Konârak	Indirect
Kaziranga National Park	No
Keoladeo National Park	No
Manas Wildlife Sanctuary	No
Churches and Convents of Goa	Indirect
Fatehpur Sikri	Indirect
Group of Monuments at Hampi	Indirect
Khajuraho Group of Monuments	Indirect
Elephanta Caves	Direct (artificial caves and rock art)
Great Living Chola Temples 12	Indirect
Group of Monuments at Pattadakal	Indirect
Sundarbans National Park	No
Nanda Devi and Valley of Flowers National Parks	No
Buddhist Monuments at Sanchi	Indirect
Humayun's Tomb, Delhi	Indirect
Qutb Minar and its Monuments, Delhi	Indirect
Mountain Railways of India	Direct (engineering geological solutions)
Mahabodhi Temple Complex at Bodh Gaya	Indirect
Rock Shelters of Bhimbetka	Direct (rock shelters, rock art)
Champaner-Pavagadh Archaeological Park	Indirect
Chhatrapati Shivaji Terminus (formerly Victoria Terminus)	Indirect
Red Fort Complex	Indirect
The Jantar Mantar, Jaipur	No
Western Ghats	No
Hill Forts of Rajasthan	Indirect
Great Himalayan National Park Conservation Area	No
Rani-ki-Vav (the Queen's Stepwell) at Patan, Gujarat	Direct (stepwell and water tank construction) and indirect

Table 2. The geological activity of humans represented in the UNESCO WHSs of India.

The list follows the web-page of the UNESCO World Heritage Centre (http://whc.unesco.org/en/list/); accessed on March 22, 2015. Evaluation is based on the official UNESCO site descriptions (the both short and long descriptions are considered) on the noted web-page. The authors' own observations in some of the listed WHS are also taken into account.



Fig. 2. Approximate distribution by age of the Indian, Italian, and Russian WHSs with direct and indirect evidence of geological activity of humans.

#### Italy

Among 50 WHSs established in Italia, 90% bear direct and/or indirect evidence of geological activity of humans and 28% bear direct evidence (Table 3). Their age varies significantly, and the prehistorical, historical, and modern time spans are represented adequately (Fig. 2). The WHSs representing ancient catacomb construction (in Historic Centre of Naples) and rock cutting, ancient mining and quarrying, workshops and stone tool production, terrace building, etc. provide bold examples of the geological activity of humans. Building large constructions and landscape modification since the Prehistoric times and, particularly, during the period of the Roman Empire and the Renaissance epoch, have affected significantly the geological environment on the territory of this country.

WHS	Evidence of geological activity of humans
Rock Drawings in Valcamonica	Direct (rock art ancient mining)
Church and Dominican Convent of Santa Maria delle	Indirect
Grazie with "The Last Supper" by Leonardo da Vinci	
Historic Centre of Rome, the Properties of the Holy See	Indirect
in that City Enjoying Extraterritorial Rights and San Paolo	
Fuori le Mura	
Historic Centre of Florence	Indirect
Piazza del Duomo Pisa	Indirect
Venice and its Lagoon	Direct (modification of geological environment)
terree and his Eugeen	and indirect
Historic Centre of San Gimignano	Indirect
The Sassi and the Park of the Rupestrian Churches of	Direct (prehistoric rock-cut settlement) and indirect
Matera	Direct (premistorie rock cut settement) and maneet
City of Vicenza and the Palladian Villas of the Veneto	Indirect
Cresni d'Adda	No
Ferrara City of the Renaissance and its Po Delta 14	Indirect
Historic Centre of Naples	Direct (catacombs) and indirect
Historic Centre of Siena	Indirect
Castal dal Monta	Indirect
Early Christian Monuments of Payonna	Indirect
Listoria Contra of the City of Dianza	Indirect
Trulli of Alborobollo	Direct (limestane dwallings) and indirect
19th Contum Royal Palace at Cocente with the Perk	Indirect (Innestone dweinings) and indirect
the A quaduat of Venuitalli, and the Sen I quais Complex.	munect
Australagical Area of Australia and the San Leucio Complex	Tu d'un et
Archaeological Area of Agrigento	Indirect
Archaeological Areas of Pompel, Herculaneum and	Indirect
Torre Annunziata	Na
Botanical Garden (Orto Botanico), Padua	NO
Cathedral, Torre Civica and Piazza Grande, Modena	Indirect
Costiera Amalfitana	Direct (terrace building) and indirect
Portovenere, Cinque Terre, and the Islands (Palmaria,	Direct (terrace building) and indirect
Tino and Tinetto)	
Residences of the Royal House of Savoy	Indirect
Su Nuraxi di Barumini	Indirect
Villa Romana del Casale	Indirect
Archaeological Area and the Patriarchal Basilica of	Indirect
Aquileia	
Cilento and Vallo di Diano National Park with the	Direct (stone tools production, landscape modification,
Archeological Sites of Paestum and Velia, and the Certosa	creation of recognizable stratigraphical
di Padula	record) and indirect
Historic Centre of Urbino	Indirect
Villa Adriana (Tivoli)	Indirect
Assisi, the Basilica of San Francesco and Other	Indirect
Franciscan Sites	
City of Verona	Indirect
Isole Eolie (Aeolian Islands)	Direct (collecting obsidian for stone tools production)
Villa d'Este, Tivoli	Indirect
Late Baroque Towns of the Val di Noto (South-Eastern	Indirect
Sicily)	
Sacri Monti of Piedmont and Lombardy	Indirect
Monte San Giorgio	No
Etruscan Necropolises of Cerveteri and Tarquinia	Direct (rock cutting) and indirect
Val d'Orcia	Direct (landscape modification and engineerin
	geological solutions) and indirect

Table 3. The geological activity of humans represented in the UNESCO WHSs of Italy.

Syracuse and the Rocky Necropolis of Pantalica	Direct and indirect (rock cutting)
Genoa: Le Strade Nuove and the system of the Palazzi	Indirect
dei Rolli	
Mantua and Sabbioneta	Indirect
Rhaetian Railway in the Albula / Bernina Landscapes	Direct (engineering geological solutions)
The Dolomites	No
Longobards in Italy. Places of the Power (568-774 A.D.)	Indirect
Prehistoric Pile dwellings around the Alps	Indirect
Medici Villas and Gardens in Tuscany	Indirect
Mount Etna	No
Vineyard Landscape of Piedmont: Langhe-Roero and	Direct (landscape modification) and indirect
Monferrato	

Table 3. continued.

The list follows the web-page of the UNESCO World Heritage Centre (http://whc.unesco.org/en/list/); accessed on March 22, 2015. Evaluation is based on the official UNESCO site descriptions (the both short and long descriptions are considered) on the noted web-page. The authors' own observations in some of the listed WHS are also taken into account.

#### Russia

Among 26 WHSs established in Russia, 65% bear direct and/or indirect evidence of geological activity of humans and 23% bear direct evidence (Table 4). The majority of them represent the time interval after 1000 AD (Fig. 2). The most impressive are the artificial landforms (e.g., mounds in the Uvs Nuur Basin). Flourishing of the Russian society since the beginning of the 2<sup>nd</sup> millennium AD led to the rise of very spectacular architecture (e.g., White Monuments of Vladimir and Suzdal) and building these churches and architectural ensembles (world-famous historical monuments nowadays) required extraction of the really huge volume of material from the geological environment.

#### Summary: relevance to the Anthropocene

Evidently, the world heritage differs significantly in India, Italy, and Russia. Among these three countries, Italy has the biggest number of WHSs (Table 3) and Russia has the smallest (Table 4); India is somewhere in between (Table 2). However, all these countries boast really rich world heritage. The number of WHSs with direct and/or indirect evidence of geological activity of humans is high in India and Italy, while it is moderate in Russia. This difference can be explained by a higher proportion of natural WHSs and a lower proportion of cultural WHSs in Russia. Anyway, all countries considered in this study possess numerous WHSs informing about anthropogenic influence on the geological environment. Moreover, these sites are essentially diverse, which means they represent different kinds of this influence (Table 2-4). If so, India, Italy, and Russia have significant potential for discussion and promotion of the Anthropocene-related issues on the basis of their world heritage.

It is important that the idea of the Anthropocene is not something too general, too qualitative, and, thus, too vague. In addition to its almost philosophical essence (CRUTZEN & SOTERMER 2000; CRUTZEN 2002; LÖVBRAND et al. 2009, 2015; BROWN 2014; DIRZO et al. 2014), it is of practical importance in modern geology because of the statigraphical value of the Anthropocene (RUBAN 2008; ZALASIEWICZ et al. 2008, 2014, 2015; WATERS et al. 2014a, 2016; see also BEACH et al. 2015). In order to use WHSs of any given country for the purposes of discussion of the rank and the boundaries of this stratigraphical unit, it is necessary to have a range of WHSs representing the time span from the very Prehistory to the Present, including WHSs dated by the 18<sup>th</sup>–20<sup>th</sup> centuries. From the three countries considered in this study, only Italy has more or less suitable WHSs with regard to their distribution by age (Fig. 2). Although Prehistorical and post-1800 AD world heritage is available in all countries, its amount is not so large. Moreover, many cultural WHSs are older than the 19th century. If so, it is possible to use WHSs of India, Italy, and Russia to argue the "early" start of the Anthropocene (via emphasis on the very strong geological activity of humans before 1800 AD) but, unfortunately, these objects are evidently not enough to discuss the start of the Anthropocene in the 19th century or later. This can be also interpreted so that the underrepresentation of the post-1800 record in the WHSs makes the relevant judgements of the Anthropocene incomplete.

An intriguing addition is possible. LEWIS & MASLIN (2015) proposed that 1610 can be a very appropriate year for the beginning of the Anthropocene (the alternative option is 1964). If so, all three countries considered in the present study provide a lot of evidence for discussion of this idea because India, Italy, and Russia have many WHSs representing the 17<sup>th</sup> century (Fig. 2). Stratigraphers dealing with the lower limit of the Anthropocene should not miss this option.

WHS	Evidence of geological activity of humans
Historic Centre of Saint Petersburg and Related Groups	Direct (modification of geological environment)
of Monuments	and indirect
Kizhi Pogost	No
Kremlin and Red Square, Moscow	Indirect
Cultural and Historic Ensemble of the Solovetsky Islands	Direct (artificial landforms, including stone labyrinths
	and fishery constructions) and indirect
Historic Monuments of Novgorod and Surroundings	Indirect
White Monuments of Vladimir and Suzdal	Indirect
Architectural Ensemble of the Trinity Sergius Lavra in	Indirect
Sergiev Posad	
Church of the Ascension, Kolomenskoye	Indirect
Virgin Komi Forests	No
Lake Baikal	No
Volcanoes of Kamchatka	No
Golden Mountains of Altai	No
Western Caucasus	Direct (megalithic constructions)
Curonian Spit	Direct (efforts to mitigate natural wind and tide erosion
	and to sustain landform)
Ensemble of the Ferapontov Monastery	Indirect
Historic and Architectural Complex of the Kazan Kremlin	Indirect
Central Sikhote-Alin	No
Citadel, Ancient City and Fortress Buildings of Derbent	Indirect
Uvs Nuur Basin	Direct (mounds)
Ensemble of the Novodevichy Convent	Indirect
Natural System of Wrangel Island Reserve	No
Historical Centre of the City of Yaroslavl	Indirect
Struve Geodetic Arc	Direct (ability of humans to measure the Earth)
Putorana Plateau	No
Lena Pillars Nature Park	No
Bolgar Historical and Archaeological Complex	Indirect

Table 4. The geological activity of humans represented in the UNESCO WHSs of Russia.

The list follows the web-page of the UNESCO World Heritage Centre (http://whc.unesco.org/en/list/); accessed on March 22, 2015. Evaluation is based on the official UNESCO site descriptions (the both short and long descriptions are considered) on the noted web-page. The authors' own observations in some of the listed WHS are also taken into account.

# **Case examples**

# India

The Ellora Caves WHS is located in the state of Maharashtra (western India) (Fig. 1). Its historical and geological contexts are discussed by SHARMA & DHAWAN (1994) and ANSARI *et al.* (2014) and also in a number of on-line sources (Appendix 1). Generally, this WHS is an example of rock-cut architecture of the 1<sup>st</sup> millennium AD. Thirty four caves were carved for religious (Buddhist, Hindu, and Jain) purposes in the Deccan basalt flows, where 'aa' and 'pahoehoe' lavas alternate. The Chitya Hall measures 26×14×10 m (SHARMA & DHAWAN 1994). The colossal size of these artificial landforms (Fig. 3), the 'physical' efforts that were necessary to cut large caves in solid volcanic rock forming the 2 km-long cliff, as well as the depth

and the complexity of the knowledge of the ancient architects (SHARMA & DHAWAN 1994) are signs of geological-scale activity of humans. Interestingly, the Ellora Caves are promoted on-line (Appendix 1) also as a tourist destination without environmental pollution, i.e., the lowest degree of anthropogenic influence is stressed in this case.

This WHS implies that humans have been significant geological agents well before the 19<sup>th</sup> century or, better to say, already in the 1<sup>st</sup> millennium AD. This is a local, but important argument for the discussion of the "early" start of the Anthropocene.

# Italy

The Cilento and Vallo di Diano National Park with the Archeological Sites of Paestum and Velia, and the Certosa di Padula WHS is located in the province of



Fig. 3. The Ellora Caves WHS: A. panoramic view; B. internal view.

Salerno (Campania, Italy) (Fig. 1). This area is very important for our knowledge of the Prehistory as it is characterized by the occurrence of cave, shelter and open-air sites, mainly situated along the rocky coast (Fig. 4, 5) (see also Appendices 2, 3). The results of the half-century-long research allowed scholars to reconstruct in detail the pre-protohistoric peopling of the region from the Lower Palaeolithic (Cala Bianca, Arconte, and Capo Grosso) (PALMA DI CESNOLA 1969a, 1976, 2001; GAMBASSINI & PALMA DI CESNOLA 1972; GAMBASSINI 1984; GAMBASSINI *et al.* 1995) to the Bronze Age (Grotta del Noglio) (VIGLIARDI 1975) in the both palaeoenvironmental and cultural perspectives. The coastal area between Scario and Camerota is of special interest. With their very thick stratigraphical sequences, several sites provided a detailed framework of the human occupation during the Middle and Upper Palaeolithic: Grotta Grande, Riparo del Molare di Scario, and Grotta/Riparo del Poggio (PAL-MA DI CESNOLA 1969b; BARTOLOMEI *et al.* 1975; GAM-



Fig. 4. Prehistoric sites located along the coast between Camerota and Scario in the Cilento and Vallo di Diano National Park (WHS) (modified from GAMBASSINI *et al.* 1995).



Fig. 5. The Cilento and Vallo di Diano National Park with the Archeological Sites of Paestum and Velia, and the Certosa di Padula WHS: A. Arconte; B. Riparo del Molare; C. Grotta della Cala; D. Grotta di Castecivita (photos from the archives of the University of Siena).

BASSINI 1995a, 2003; CARAMIA & GAMBASSINI 2006) for the Middle Palaeolithic, Grotta della Serratura (MARTINI 1993, 1995) for the Upper Palaeolithic and the Holocene, Grotta della Cala, (PALMA DI CESNOLA 1971; GAMBASSINI 1995b; BENINI *et al.* 1997; BOSCA-TO *et al.* 1997; BORGIA & WIERER 2005; BORGIA 2008; MORONI *et al.* in press) for the Middle-Upper Palaeo-lithic and the Holocene. Additionally, interesting human remains like the Neandertal juvenile mandible are available from Riparo del Molare (MALLEGNI & RON-CHITELLI 1987, 1989; RONCHITELLI 1993, 1995a,b).

Grotta della Cala was occupied, with few interruptions, from the final Middle Palaeolithic to the Copper Age. During the Palaeo-Mesolithic human occupation, the sea level was lower than nowadays (LAMBECK *et al.* 2011) and a flat land-belt was present in front of the cavity. The stratigraphical sequence of Grotta della Cala starts with a marine strongly cemented conglomerate (MIS 5). This is followed by a set of intercalating stalagmite and gravel layers belonging to the final Mousterian sealed by a thick "concretion" layer constituting the base of the Upper Palaeolithic sequence (Uluzzian, Aurignacian, Early Gavettian, Evolved Gravettian with few Noailles-type Burins, Evolved and Final Epigravettian), which is overlain by the Holocene sequence (Mesolithic, Neolithic and Eneolithic). One of the more interesting aspects of Grotta della Cala is the presence of layers, which document the earliest phases of the Upper Palaeolithic, namely the Uluzzian and the Aurignacian techno-complexes. This particular period, known as the Middle to Upper Palaeolithic transition, is currently the object of an international debate as it involves the demise of last Neandertal populations and their gradual replacement by the Modern Humans (Homo sapiens) between 45 and 40 ka (BENINI et al. 1997; MORONI et al. 2013). This intriguing aspect of the Italian Palaeolithic occurs also on another site, namely the Grotte di Castelcivita. This is a karst cavity, develops more than 4 km horizontally and about half of which can be visited by the public. The Palaeolithic site occupies the mouth of the cave. The stratigraphical sequence starts with a thick layer of blocks collapsed during a rather cold phase at  $\sim 60-50$  ka. In the overlying layers, there is evidence of the occupation by last Neandertals (~ 45 ka), divided by a stratigraphic hiatus from the overlying Uluzzian (~ 41 ka) and Protoaurignacian (~ 40 ka) techno-complexes.

The cave was later invaded at  $\sim 39$  ka by the dusts of a violent volcanic eruption (Campanian ignimbrite) (GAMBASSINI 1995c, 2000).

Generally, this Italian WHS is important for the Anthropocene-related knowledge because it provides the precious technological information on the exploitation of lithic resources for stone tool production and landscape modification (creation of cultural landscapes and cultural exploration of such notable geomorphological objects as caves) by Neandertals and especially Modern Humans in the Prehistory, as well as on the creation of outstanding stratigraphical record of the past human activity (in other words, the anthropogenic deposits of geological scale appeared) (Appendices 2, 3). Moreover, the interaction between the geological forces (karst, volcanism, etc.) and the past human activity is visible there.

Another example of the Italian WHSs of the Anthropocene-related importance is the Aeolian (Lipari) Islands, which are located in the Tyrrhenian Sea to the north of Sicily (Fig. 1). From the Neolithic (but not during the Palaeolithic) these were permanently occupied by human communities. The economic and cultural growth of this archipelago during the Neolithic was partly due to the exploitation of obsidian. This natural material is very suitable for knapping, and it was especially used for making sharp edged blades. Because of its characteristic and its fine bright appearance, it was largely exported in the Prehistory, and small quantities of obsidian often travelled (as a kind of "exotic" goods) over large distances. Since obsidian occurs on only four islands (Sardinia, Palmarola, Lipari, and Pantelleria) in the Central-Western Mediterranean, this material is of broad interest for provenance studies: its physical and chemical properties can be used to discriminate the raw material natural sources and, as a consequence, to correlate artefacts retrieved in prehistoric sites to the supplying outcrops. At Lipari, the largest of the seven islands of the Aeolian Archipelago, there are several obsidian outcrops (including Forgia Vecchia, Pomiciazzo or Gabellotto, Canneto Dentro, and Rocche Rosse), the formation of which is due to a number of volcanic events that took place between 11.4 ka and 1.4 ka (BIGAZZI et al. 2005). Pomiciazzo and Canneto Dentro are the only outcrops showing a chronology consistent with their potential exploitation in Prehistory. Obsidian from Lipari started circulating systematically in Southern Italy from the Early Neolithic. During the Middle Neolithic (phase of the Tricromic and Serra d'Alto painted pottery), there was an increase in circulation and the widest distribution network of obsidian from Lipari. This moved up peninsular Italy and reached the Northern regions where it can be often found in association with obsidian from Palmarola and Monte Arci. Many V millennium BC artefacts (usually finished products - see VAQUER 2006) obtained from Lipari obsidian are found in Malta, Southern France (VAQUER 2003), and Istria (Тукот et al. 2013).

The Aeolian Islands WHS is important for the Anthropocene-related knowledge because it provides direct evidence of geological activity of Prehistoric humans linked to obsidian collecting. This was a primitive form of mining. However, a very significant amount of collected obsidian that can be deduced from its wide distribution in the Mediterranean and, particularly, on the Italian territory implies that this mining was massive and that those Prehistoric humans acted as true geological agents.

# Russia

The Cultural and Historic Ensemble of the Solovetsky Islands WHS is located on the Solovetsky Archipelago in the White Sea in the Arkhangel'sk Region (northwestern Russia) (Fig. 1). It was known mainly because of the famous monastery founded in the 15<sup>th</sup> century and flourished in the 16<sup>th</sup> century, as well as by the tragic events of the 20<sup>th</sup> century. However, this WHS includes also some cultural elements that are of geoarchaeological and geomorphological importance (Appendix 4). Firstly, these are dozens of the stone labyrinths, cairns, and other megalithic constructions on the Big Zayatsky and Anzer islands. Labyrinths (locally called "Babylons") were built with local boulders in the 3<sup>rd</sup> millennium BC; on the Big Zayatsky Island, these concentrate on the area of only 0.4 km<sup>2</sup> in size, and their purpose is far from being fully understood. Secondly, fishery constructions (so-called "Philip's ponds") of the 16<sup>th</sup> century are of interest. These are shallow ponds (not longer in use) divided by dams on the seashore of the Solovetsky Island. The dams were constructed from large granitic boulders with smaller boulders in between. Generally, these fishery constructions changed the natural seashore landscape completely, and they represent the highly specific artificial landform. Their building required extraction and transportation of a huge amount of natural stones, as well as engineering geological solutions for seashore modification. Both kinds of cultural elements of this WHS stress the geological-scale activity of humans in the prehistorical and historical times. With regard to the idea of the Anthropocene, this conclusion does not support the idea that the geological power (with regard to the ability of landscape modification) of the prehistorical societies was lesser than that in the historical times. Locally, the Anthropocene started well before the 19<sup>th</sup> century.

The Historic and Architectural Complex of the Kazan Kremlin is located in the city of Kazan in the Republic of Tatarstan (European part of Russia) (Fig. 1). It combines elements belonging to the culture of the Volgian Bulgars, the Golden Horde, the Medieval Kazan Tatars, the Russians, and the modern Tatars (Fig. 6). Generally, the Kazan Kremlin is preserved substantially since its last major reconstruction after



Fig. 6. The Historic and Architectural Complex of the Kazan Kremlin WHS: **A**, **B**. general views; **C**. masonry of the Khan's period (15th–mid-16th centuries); **D**. masonry used by Pskov architects (1556–1562).

the conquest of the Kazan Khanate by Ivan IV in 1552. During 1556–1562, the fortress walls and towers were built by Pskov architects from "white stone". The latter is the Late Kazanian (Roadian, Middle Permian; see MENNING et al. 2006) light-gray dolostones and limestones. These rocks are exposed in the coastal cliffs on the right bank of the Volga River, from where they had been extracted and transported to the Kazan Kremlin together with the stones from the pre-Mongolian destroyed buildings dating back to the 12th century (SITDIKOV 2009). The masonry of the Khan's period (15<sup>th</sup>-mid–16<sup>th</sup> centuries) is characterized by almost complete absence of mortar (Fig. 6). Later, the Pskov masters used a solid fill with mortar from the outer to the inner edge of the wall (KHUZIN 2001). The space between the outer blocks was filled with relatively large rough stones. Some towers of the second half of the 16th century were built on the ruins of the towers of the Khan's period (KHUZIN 2001). They were built as monoliths by pouring of large limestone and dolostone hewn blocks and fragments of brick with mortar. Blocks were obtained by dismantling of the masonry of the earlier square tower.

The site described above is a typical example of WHS with indirect evidence of the geological activity

of humans: the multi-stage building of the Kazan Kremlin required extraction of a huge amount of geological material (carbonate rocks) from the nearby outcrops. Besides this, one should expect significant modification of local landforms, because this extraction led to the destruction of the natural cliffs, where these rocks are exposed. The evidence is indirect because one needs special interpretation (and "deep thinking") of signs available at the site itself. In other words, geological activity of man can be only imagined, not viewed directly there. With regard to the Anthropocene, this WHS provides an additional argument for its "early" start in the Volga region of Russia.

#### **Summary of case examples**

The five representative examples of the WHSs from India, Italy, and Russia discussed above allow conclusionsabout the geological activity of humans in both prehistorical and historical times (Fig. 7). The most impressive among them is the Ellora Caves WHS in India because it permits to judge about the outstanding potential of past civilizations to affect the geological environment. However, the only "early" start of the Anthropocene can be discussed considering all these sites, because they represent the time before the 19<sup>th</sup> century (Fig. 7).



Fig. 7. The WHSs considered in the present study along the geological timeline.

# Conclusions

The present study of the WHS importance for accumulation and promotion of the Anthropocene-related knowledge in three heritage-rich countries, namely India, Italy, and Russia, permits to make three general conclusions:

1) the studied countries have many WHSs with the direct and indirect evidence of the geological activity of humans and, thus, these are appropriate for general discussion and promotion of the idea of the Anthropocene;

2) the world heritage available in India, Italy, and Russia permits discussion about an "early" (pre-1800 AD) start of the Anthropocene, but it is much less suitable for the analysis of anthropogenic influence on the geological environment in the 19<sup>th</sup> century and later;

3) some WHSs taken alone (e.g., the Ellora Caves in India) are of utmost importance to realize the geological scale of the human activity.

Future studies should consider more countries in order to extend the conclusions made on the basis of information from India, Italy, and Russia. Special attention should be paid to tourism programs offered at WHSs in order to understand their true importance for effective promotion of the Anthropocene-related knowledge.

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elloracaves.org maharashtratourism.gov.in sacred-destinations.com whc.unesco.org

Appendix 2. On-line information sources on the Cilento and Vallo di Diano National Park.

lonelyplanet.com/italy/campania/parco-nazionale-delcilento-e-vallo-di-diano

europeangeoparks.org/?page id=561

italia.it/en/travel-ideas/unesco-world-heritagesites/cilento.htm

whc.unesco.org

Appendix 3. Geoarchaeological sites of the Cilento and Vallo di Diano National Park (listed in chronological order).

- *Cala Bianca* (oper-air site): Lower Palaeolithic (Acheulean) (PALMA DI CESNOLA 1969a, 1976, 2001; GAMBASSI-NI & PALMA DI CESNOLA 1972; GAMBASSINI 1984; GAM-BASSINI *et al.* 1995).
- Arconte and Capo Grosso (open-air sites): Lower Palaeolithic (Acheulean) (PALMA DI CESNOLA 1969a, 1976, 2001; GAMBASSINI & PALMA DI CESNOLA 1972; GAM-BASSINI 1984; GAMBASSINI et al. 1995).
- Grotta and Riparo del Poggio (cave and shelter sites): Middle Palaeolithic (PALMA DI CESNOLA 1967, 1969b, 2001; GAMBASSINI 1995a; CARAMIA & GAMBASSINI 2006).
- *Grotta di Porto Infreschi* (collapsed cave): Middle Palaeolithic (SARTI 1995).
- Grotta Grande (cave site): Middle Palaeolithic (RONCHI-TELLI 1995b).
- *Riparo del Molare* (shelter site): Middle Palaeolithic (MALLEGNI & RONCHITELLI 1987, 1989; RONCHITELLI 1993, 1995a).

- *Grotta Tina* (cave site): Middle Palaeolithic (MARTINI *et al.* 1972-74; GAMBASSINI *et al.* 1995).
- *Grotta Taddeo* (cave site): Middle Palaeolithic (VIGLIARDI 1968; GAMBASSINI *et al.*1995).
- *Nicchia Silhar* (shelter site): Middle Palaeolithic (GAM-BASSINI *et al.*1995).
- *Riparo della Difesa* (shelter site): Middle Palaeolithic (GAMBASSINI *et al.*1995).
- *Grotta dell'Acqua* (cave site): Middle Palaeolithic (GAM-BASSINI *et al.*1995).
- *Grotta della Masseta* (cave site): Middle Palaeolithic (GAMBASSINI *et al.*1995).
- *Grotte di Castelcivita* (cave site): Middle Palaeolithic, Upper Palaeolithic (Uluzzian, Proaurignacian) (GAMBASSI-NI 1995c, 2000).
- *Grotta della Serratura* (cave site): Middle Palaeolithic, Upper Palaeolithic (Gravettian, Epigravettian), Mesolithic (Sauveterrian), Neolithic (MARTINI 1993, 1995).
- Grotta della Cala (cave site): Middle Palaeolithic, Upper Palaeolithic (Uluzzian, Aurignacian, Gravettian, Epigravettian), Mesolithic (Sauveterrian), Neolithic, Eneolithic (PALMA DI CESNOLA 1967, 1971; BARTOLOMEI et al. 1975; MARTINI 1978, 1981; GAMBASSINI 1995, 2003; BE-NINI et al. 1997; BOSCATO et al. 1997; GAMBASSINI & RONCHITELLI 1997; BORGIA & WIERER 2005; BORGIA 2008; MORONI et al. in press).
- Grotta Calanca (cave site): Upper Palaeolithic (Gravettian) (VIGLIARDI 1968b; BACHECHI & REVEDIN 1993; GAM-BASSINI et al. 1995).
- Grotta Santa Maria (cave site): Upper Palaeolithic (Epigravettian) (BACHECHI 1989-90; GAMBASSINI *et al.* 1995).
- *Grotta del Noglio* (cave site): Bronze Age (VIGLIARDI 1975; GAMBASSINI *et al.* 1995).
- Grotta di Cascarella (cave site): Bronze Age (GAMBASSINI et al., 1995).

Appendix 4. On-line information sources on the labyrinths and the fishery constructions of the Cultural and Historic Ensemble of the Solovetsky Islands.

dic.academic.ru karelia-lines.ru my-solovki.ru redigo.ru sciteclibrary.ru solovki-monastyr.ru turizm.ru whc.unesco.org

# Резиме

# Геолошка активност човека представљена на локалитетима светске баштине у Италији, Индији и Русији: докази антропоцена

Антропоцен представља релативно нови концепт али је већ привукао пажњу великог броја

истраживача. У првом реду, антропоцен одражава геолошку (укључујући и геоморфолошку) активност човека. Осим тога, термин антропоцен има и стратиграфско значење: појављује се на геолошкој скали као нова епоха или као формална/неформална јединица другог реда. Најупечатљивији докази о постојању антропоцена долазе са простора који истовремено пружају геолошке и културолошке податке, при чему су локалитети на листи светске баштине УНЕСКА од највећег значаја. Главни циљ овог рада је да пружи преглед доступних података са локалитета под заштитом УНЕСКА који се налазе у три земље са богатом културном и природном баштином тј. Индији, Италији и Русији који се односе на геолошку активност човека, у циљу дефинисања њиховог значаја за боље разумевање антропоцена. Истраживања за потребе овог рада спроведена су током четири фазе. Прво је установљено присуство различитих трагова геолошке активности човека везане за локалитете светске баштине (ЛСБ) у свакој од три наведене земље како би се утврдили директни или индиректни докази ове активности. Затим је утврђено време геолошког деловања човека везано за сваки од истраживаних локалитета. У трећој фази истраживања коришћене су две аналитичке методе. Израчунат је процентуални однос директних и индиректних доказа о геолошкој активности човека добијених на одређеном броју локалитете светске баштине у свакој од земаља. Утврђено је и оквирна старост геолошке активности човека значајне за сваки од истраживаних локалитета. На основу тога изведени су закључци о значају ових доказа и њиховој релевантности за концепт антропоцена. У четвртој фази су детаљно анализирани репрезентативни примери ЛСБ који су потенцијално значајни за даљи развој концепта антропоцена. Од укупно 32 ЛСБ рагистрована у Индији, 75% пружа директне и/или индиректне а 22% директне доказе доказе геолошке активности човека. Од 50 ЛСБ у Италији, 90% носи директне и/или индиректне доказе геолошке активнсти човека, а 28% локалитета пружа директне доказе. На 26 ЛСБ у Русији, директни и/или индиректни докази геолошке активнсти човека пронађени су на 65% локалитета, а 23% локалитета пружа директне доказе. Анализа локалитета светске баштине на тлу Индије, Италије и Русије показује да ове земље генерално имају велики значај за разматрање проблема везаних за антропоцен, као и за даљи развој овог концепта. Локалитети светске баштине у наведеним земљама могу бити коришћени као аргумент за "рани" почетак антропоцена (на основу значајне геолошке активности човека пре 1800. г.н.е.) али, нажалост, ови објекти дефинитивно не пружају довољно аргумената за дискусију о почетку антропоцена у 19. веку или касније. Елора пећине, ЛСБ у за-
падној Индији, указује на то да је човек био значајан геолошки фактор далеко пре 19. века или, боље речено, већ у првом миленијуму нове ере. Иако је реч о једном локалитету, ово представља важан аргумент за дискусију о "раном" почетку антропоцена. Национални парк Ћиленто и Вало ди Дано, ЛСБ у Италији са локалитетима Пестум, Велиа и Кертоса ди Падула, пружа драгоцене информације о технологији експлоатације стенских материјала за потребе израде камених оруђа, о морфолошким изменама предела од стране неандерталаца а нарочито модерног човека у праисторији, као и изузетно важне стратиграфске податке о некадашьој активности човека. Историјски и архитектонски комплекс Казњски Кремљ у Русији представља типичан пример ЛСБ са индиректним доказима геолошке активности човека: вишефазна изградња Казањски Кремља захтевала је екстракцију огромне количине геолошког материјала (карбонатних стена) са оближњих локалитета. На основу пет репрезентативних примера ЛСБ на територијама Индије, Италије и Русије могуће је донети закључке о геолошкој активности човека, како у периду праисторије тако и током историје. Ипак, на основу поменутих локалитета може се дискутовати само о "раном" почетку антропоцена. Даља истраживања би требало да укључе више земаља како би се допунили закључци добијени на основу информација из Индије, Италије и Русије. Нарочиту пажњу би требало посветити туристичким програмима који се нуде на ЛСБ како би се боље разумео њихов прави значај у стицању нових сазнања везаних за антропоцен.

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AGER, D.V. 1963. *Principles of Paleoecology*. 318 pp. McGraw-Hill, New York.

- OWEN, E.F. 1962. The brachiopod genus Cyclothyris. Bulletin of the British Museum (Natural History), Geology, 7 (2): 2–63.
- RABRENOVIĆ, D. & JANKIČEVIĆ, J. 1984. Contribution to the study of Albian near Topola. *Geološki anali Balkanskoga poluostrva*, 48: 69–74 (in Serbian, English summary).
- SMIRNOVA, T.N. 1960. About a new subfamily of the Lower Cretaceous dallinoid. *Paleontologicheskii Zhurnal*, 2: 116–120 (in Russian).
- SULSER, H. 1996. Notes on the taxonomy of Mesozoic Rhynchonellida. *In*: COOPER, P. & JIN, J. (eds.), *Brachiopods*, 265–268. Balkema Press, Rotterdam.

Acknowledgments should be as short and concise as possible.

A **summary** (up to 15% of the paper) is published in Serbian and should contain the essence of all new data and the conclusions.

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## ГЕОЛОШКИ АНАЛИ БАЛКАНСКОГА ПОЛУОСТРВА

ANNALES GÉOLOGIQUES DE LA PÉNINSULE BALKANIQUE



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