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Was there more space in the late Early Devonian for marine biodiversity to peak than in the early Late Ordovician?: A brief note

Dmitry A. Ruban[1]

Abstract. After the so-called “Cambrian explosion”, marine biodiversity peaked either in the early Late Ordovician (as shown by the “classical” curves based on the extensive palaeontological data compilation) or in the late Early Devonian (as shown by the “innovative” curve based on the sampling standardization). The brief review of the modern plate tectonic, palaeoclimatic, and eustatic reconstructions demonstrates that shelves, which likely provided the main space for biotic radiation, shrank, concentrated in the tropics, and were better connected in the late Early Devonian than in the early Late Ordovician. The results of the present analysis permit to hypothesize that there was more (or the same) space for marine organisms to reach their maximum in their number in the early Late Ordovician relatively to the late Early Devonian. This is the only particular hypothesis, and the other extrinsic and intrinsic factors should be considered in further discussions.

Key words: marine biodiversity, shelf, biotic radiation, Late Ordovician, Early Devonian.

Апстракт. После тзв. ”камбријумске експлозије“, морски биодиверзитет достиже свој максимум или у доњем делу горњег ордовицијума (као што је приказано ”класичном“ кривом заснованој на компилацији исцрпних палеонтолошких података) или у горњем делу доњег девона (што је приказано кривом заснованој на стандардном узорковању). Преглед података који се односе на савремену тектонику плоча, палеоклиму и реконструкцију нивоа мора, указује на смањење распространјења шелфова, који су највероватније чинили главну средину за биотску радијацију. Шелфови су били ограничени на тропске пределе и били су боље повезани у горњем делу доњег девона него у доњем делу горњег ордовицијума. Резултати добијени у овом раду дозвољавају претпоставку да су морски организми имали више, или барем подједнако простора за достизање максимума своје бројности у доњем делу горњег ордовицијума него у горњем делу доњег девона. Ово је свакако само једна од претпоставки, а у будућим анализама биће разматрани и остали спољашњи и унутрашњи фактори.

Кључне речи: морски биодиверзитет, шелф, биотска радијација, горњи ордовицијум, доњи девон.

Introduction

The new reconstruction of the global Phanerozoic marine biodiversity dynamics (Alroy *et al.* 2008) has not only changed our understanding of the history of life, but it has posed new questions. One of the most important is about the Paleozoic diversity maxima. The “classical” curves (based on the latest version of the compendium by Sepkoski (2002)) depicting changes in the number of genera through the geologic time (e.g., Purdy 2008; Aberhan & Kiessling 2012) demonstrate clearly that the first outstanding maximum in the diversity of marine invertebrates after the famous “Cambrian explosion” (see review and synopsis of the key literature sources in Ruban 2010) was reached in the early Late Ordovician (Fig. 1A). Evidently, this peak was a quintessence of the Ordovician radiation (see reviews in Harper 2006; Servais *et al.* 2009; Ruban 2010; Miller 2012). In contrast, the “innovative” curve based on the sampling standardization (Alroy *et al.* 2008) postdates such a maximum by ~50–60 Ma and places it into the late Early Devo-

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nian (Fig. 1B), when another major biotic radiation culminated (RUBAN 2010). Although the both recognized events were true diversity peaks (see the curves based on the SEPKOSKI (2002)'s compendium (PURDY 2008; ABERHAN & KIESSLING 2012; ABERHAN *et al.* 2012) and the sampling standardization (ALROY *et al.* 2008)) resulted from major radiations in the marine realm (RUBAN 2010), it remains uncertain which of them was really bigger (Fig. 1).

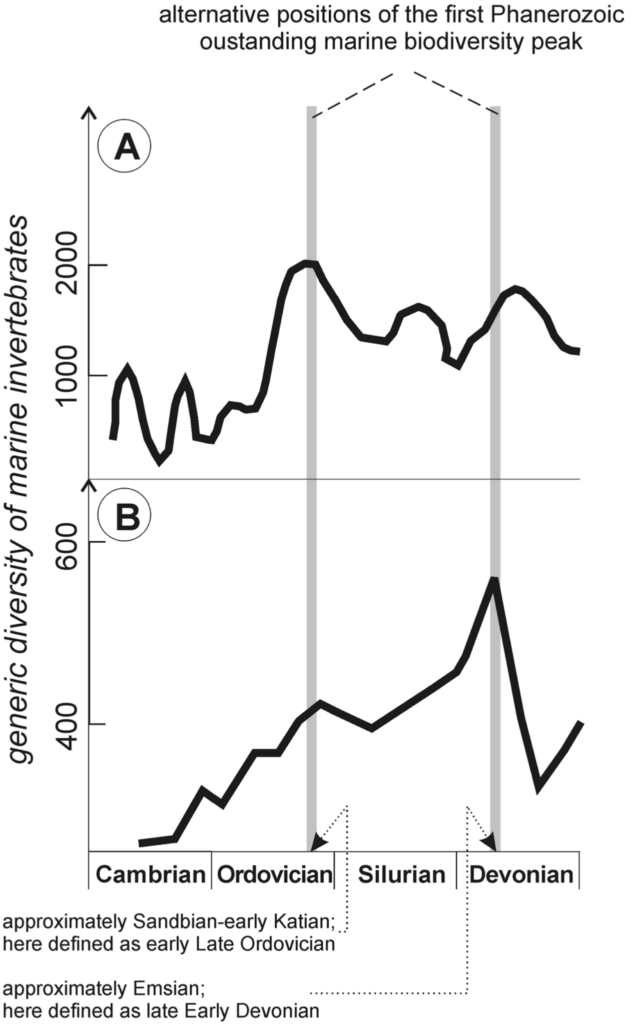

Fig. 1. Early–Middle Paleozoic marine biodiversity dynamics: **A,** "classical" diversity curve adapted from PURDY (2008) and based on the dataset by SEPKOSKI (2002); **B,** "innovative" curve adapted from ALROY *et al.* (2008) and based on sampling standardization. The scale of this figure and the correspondence of the curves follow RUBAN (2010).

The controversy between the two above-mentioned curves (or, better to say, data and approaches employed for their construction) is difficult to judge about, particularly because of different "philosophies" existing in the modern palaeobiology (e.g., BENTON 2011; RUBAN 2012). However, the discussion can be started from the "back" side, i.e., with evaluation of conditions that were or were not able to sustain higher marine biodiversity in the early Late Ordovician and the late Early Devonian. In the present note, the palaeoenvironments favourable for marine taxa to peak in their number in these two time slices are compared qualitatively. Of course, the outcome of such an analysis can be only hypothetical and particular. But even if this cannot resolve the above-mentioned controversy, the development of agenda for further investigations will be facilitated.

What space did the marine biodiversity need to peak?

Links between the space in oceans and seas that allowed marine biota to evolve and the diversity of this biota were probable, although this idea is addressed critically in the modern palaeobiological literature (ABERHAN & KIESSLING 2012; SMITH & BENSON, 2013). Generally, shelfal environments seem to be the most favourable for high biodiversity levels. On a global scale, their size depended on fragmentation of land masses, curvature of continental slopes, and sea level (ABERHAN & KIESSLING 2012; see also discussion by HOLLAND 2012). However, the existence of such a space did not necessarily lead to biodiversity acceleration. At least, two important constraints should be considered. The first constraint is climate. If warm seawater of the tropics was chiefly responsible for marine biodiversity, the only concentration of shelves near the Equator enlarged the latter. But there is an alternative point of view, which links higher number of taxa to palaeoclimatic differentiation (VALENTINE 1968; TROTTER *et al.* 2008; RUBAN 2010). In this case, the proportional pole-to-equator distribution of shelves was favourable for higher diversity. The second constraint is shelf connectivity. One may propose that either dispersal or isolation of marine organisms might have been a factor of their radiation (e.g., see RUBAN 2010). This means that the global connectivity of shelves or, in contrast, their separation by abyssal (*sensu lato*) domains might have enhanced peaks in the marine biodiversity.

The above said allows to compare the early Late Ordovician and the late Early Devonian global palaeoenvironments by the relative size, pole-to-equator distribution, and connectivity of shelves. Evidently, the uncertain importance of shelfal space for marine biodiversity to peak (ABERHAN & KIESSLING 2012), the complex relationships between the habitat size, sea-level changes, and biotic evolution (HOLLAND 2012), as well as the above-mentioned alternative interpretations of the constraints of space-biodiversity links should be further taken into account.

Comparison of two time slices

The available plate tectonic reconstructions (Scotese 2004; see also Cocks & Torsvik 2002; Lawver *et al.* 2002; Stampfli & Borel 2002; Torsvik & Cocks 2004; von Raumer & Stampfli 2008; Nance *et al.* 2012; Stampfli *et al.* 2013; see also scotese.com and ww2.nau.edu/rcb7/globaltext2.html) demonstrate that the fragmentation of land masses in the early Late Ordovician and the late Early Devonian was more or less comparable; and the degree of this fragmentation can be judged moderate (Ruban 2010). There were one large supercontinent of Gondwana and some other more or less "dispersed" middle-sized tectonic blocks in the both time slices (Fig. 2). Although Baltica and Laurentia already formed the continent of Laurussia in the Early Devonian (Stampfli & Borel 2002; Cocks & Torsvik 2005, 2011; Stampfli *et al.* 2013), and the Galatian terranes did not separate from Gondwana until the mid-Paleozoic (von Raumer & Stampfli 2008; Stampfli *et al.* 2013), there were the other relatively large and separate land masses, i.e., the Hunic terranes (von Raumer & Stampfli 2008; Stampfli *et al.* 2013) or the Kazakh continent with the related terranes (Wilhem *et al.* 2012).

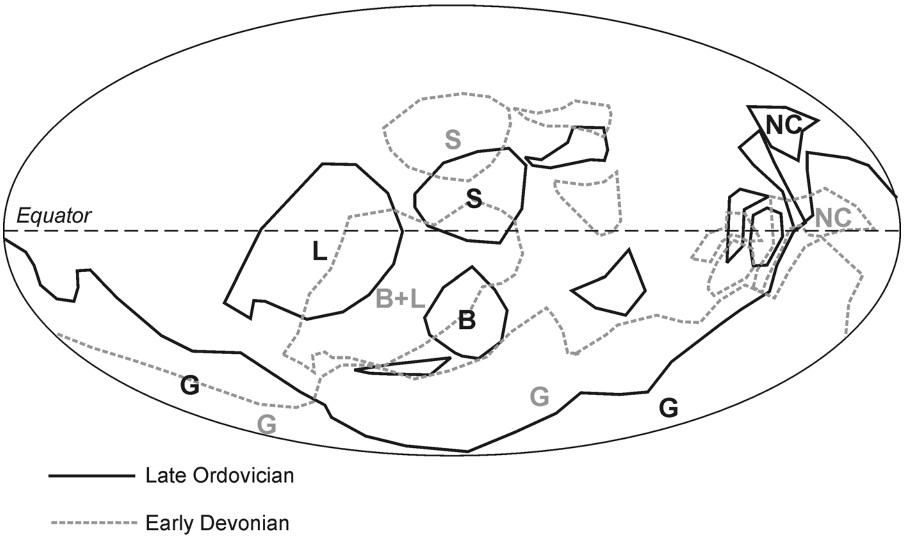

Fig. 2. Overlapped Late Ordovician and Early Devonian contours of the principal continental blocks (strongly generalized from Scotese 2004). Abbreviations: **B,** Baltica; **G,** Gondwana; **L,** Laurentia; **NC,** North China; **S,** Siberia (**B+L,** Baltica and Laurentia joined in the mid-Paleozoic to form Laurussia).

The same plate tectonic reconstructions (Cocks & Torsvik 2002, 2013; Lawver *et al.* 2002; Stampfli & Borel 2002; Scotese 2004; Torsvik & Cocks 2004; von Raumer & Stampfli 2008; Nance *et al.* 2012; Wilhem *et al.* 2012; Stampfli *et al.* 2013) permit to conclude about the comparable ratio between "active" and "passive" continental margins in the early Late Ordovician and the late Early Devonian. It can be assumed that the curvature of continental slopes, which is often controlled tectonically, was more or less similar on a global scale in these two time slices. Therefore, the established fragmentation of land masses and the curvature of continental slopes imply together the comparable size of shelfal environments in the analyzed time slices.

In contrast, significant difference is found with regard to the third factor affecting the size of shelves, i.e., the global sea level. The new eustatic reconstruction proposed by Haq & Schutter (2008) shows that this level was up to 200–220 m above the Present or even more in the early Late Ordovician, but it dropped by more than 1.5 times in the late Early Devonian, i.e., to only 120–140 m above the Present. This means that the shelfal environments in the former time slice were likely significantly larger. There were neither increase in the land mass fragmentation nor the smoothening of the continental slopes that would recompense the lower position of the global sea level in the late Early Devonian in comparison with the early Late Ordovician. Interestingly, the global palaeogeographical reconstructions by R.C. Blackey (available on-line at ww2.nau.edu/rcb7/globaltext2.html) demonstrate certain rise of the Gondwanan shelves in the Early Devonian; if so, the only moderate (if any) reduction of shelfal environments should be postulated for this time slice.

The knowledge on the early Late Ordovician climate remains controversial in somewhat (Miller 2012). It is more or less proven that the global temperature at the beginning of the Late Ordovician was high (e.g., see Fig. 8 in Zalasiewicz 2012). However, the cooling trend established by Trotter *et al.* (2008) and Boucot *et al.* (2009) and the evidence of glaciations that developed already since the Early Ordovician (Turner *et al.* 2011, 2012) imply that the Late Ordovician water masses were not exceptionally warm. It is not excluded, however, that the cooling trend was superimposed by a warming episode (Boucot *et al.* 2003; Fortey & Cocks 2005). In the late Early Devonian, the temperatures, including the low-latitude seawater surface temperatures, were high enough (Joachimski *et al.* 2009; Fig. 8 in Zalasiewicz 2012). However, the long-term cooling trend is interpreted (Joachimski *et al.* 2009). Finally, the equator-to-pole climatic gradient remained moderate in the both early Late Ordovician and the late Early Devonian (BOUCOT 2009). Speaking generally, the compared time slices were characterized by generally similarly global climatic conditions, and some pole-to-equator climatic differentiation was typical to the both of them. Evidently, it is important to realize whether there were differences in the pole-to-equator distribution of shelves between the two analyzed time slices. These can be deduced from the above-mentioned plate tectonic reconstructions (COCKS & TORSVIK 2002, 2013; LAWVER *et al.* 2002; STAMPFLI & BOREL 2002; SCOTESE 2004; TORSVIK & COCKS 2004; VON RAUMER & STAMPFLI 2008; NANCE *et al.* 2012; WILHEM *et al.* 2012; STAMPFLI *et al.* 2013). In the early Late Ordovician, the Gondwanan margin stretched from very high to very low latitudes in the Southern Hemisphere (and even entered the Northern Hemisphere), whereas separate middle-sized tectonic blocks were situated near the Equator. In the late Early Devonian, the Gondwanan margin remained large, but the interiors of the supercontinent occupied high latitudes of the Southern Hemisphere. In other words, the margin "shifted" towards Equator. The other tectonic blocks remained in the tropics with just a certain shift northwards. Therefore, it appears that the concentration of shelfal environments in the tropics increased together with the above-mentioned plate tectonic changes in the late Early Devonian relatively to the early Late Ordovician (Fig. 2). Of course, a portion of shelves remained in temperate and even high latitudes. Moreover, the global palaeogeographical reconstructions by R.C. BLACKEY (available on-line at ww2.nau.edu/rcb7/globaltext2.html) show that the Late Ordovician shelves of Gondwana also concentrated in the tropics, and they were narrower or lacking in the higher latitudes; the Early Devonian shelves of Gondwana, in contrast, were abundant in temperate latitudes. Consequently, it is sensible to suppose the only moderate (or even little) difference in the pole-to-equator distribution of shelves between the two analyzed time slices.

The connectivity of shelves changed through the early Paleozoic. At least, three features provide an evidence of its increase in the late Early Devonian in comparison to the early Late Ordovician. These include 1) the more "compact" grouping of land masses (e.g., SCOTESE 2004; STAMPFLI *et al.* 2013); 2) the shrinkage of the water space between Gondwana and Laurussia (DOJEN 2009), although the closure of the Rheic Ocean lasted through the Devonian and later (NANCE *et al.* 2012); 3) the lower global sea level (HAQ & SCHUTTER 2008).

Making hypotheses

The evidence presented above can be summarized as follows (Table 1). The global shelfal environments shrank, shifted towards Equator, and became better connected in the late Early Devonian relatively to the early Late Ordovician. If the very assumption that these environments provided the essential space for

Table 1. Comparison of global parameters considered in this paper (see text and RUBAN (2010) for more details and data sources).

Parameter	*early Late Ordovician (O3)*	*late Early Devonian (D1)*	*Comparison*
Fragmentation of land masses	moderate	moderate	O3 ≈ D1
Anticipate curvature of continental slopes			O3 ≈ D1
Global sea level	200–220 m above the Present	120–140 m above the Present	O3 > D1
Shelfal environments			O3 > D1
Climate (thermal regime)	moderately warm	moderately warm	O3 ≈ D1
Equator-to-pole climatic gradient	moderate	moderate	O3 ≈ D1
Pole-to-equator distribution of shelves	~ equal	certain concentration near the Equator	shelves in the tropics: O3 = D1
Connectivity of shelves	moderate	higher than moderate	O3 < D1

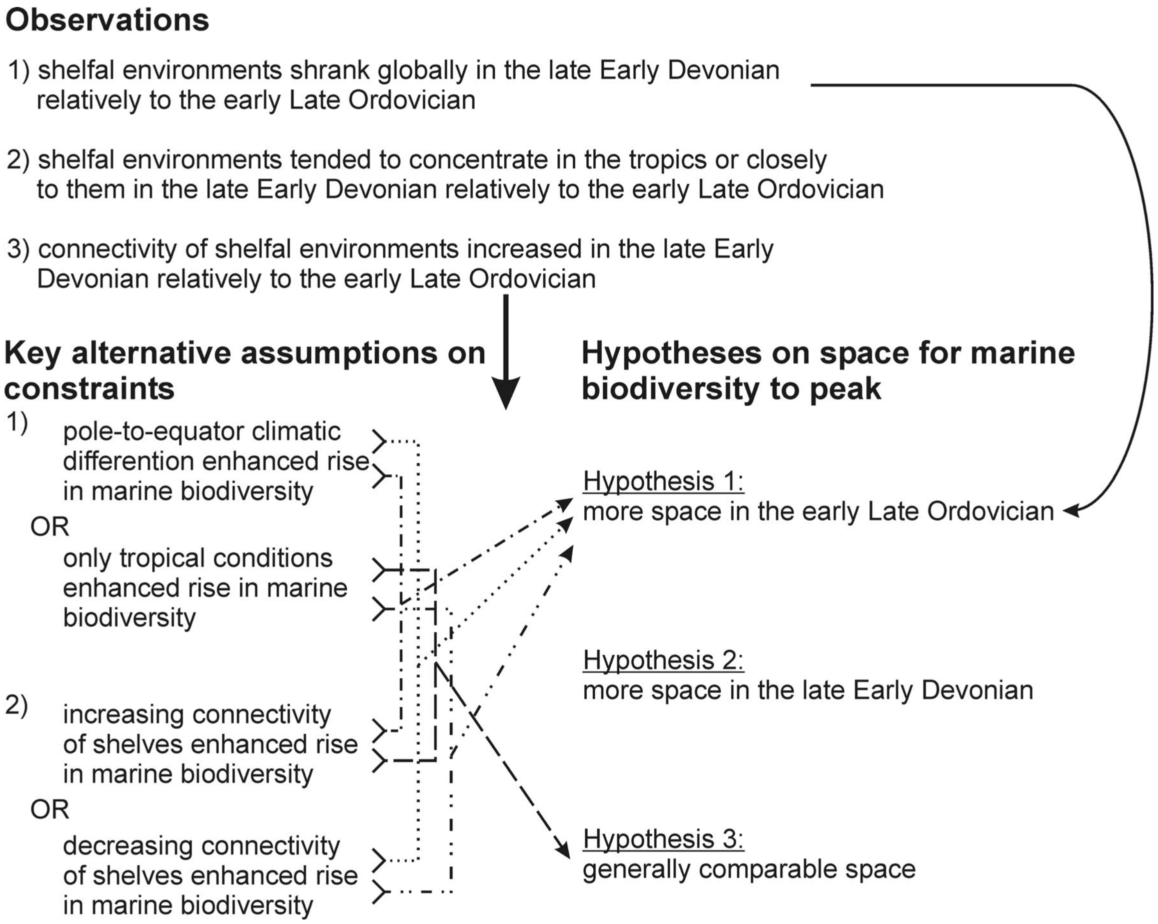

Fig. 3. Hypotheses that can be made based on the assumptions and the evidence employed in this paper (see text and Table 1). These considerations are sensible only if pole-to-equator distribution and connectivity of shelfal environments were true constraints and their importance was comparable.

the marine biodiversity to peak is valid, only two hypotheses can be proposed (Fig. 3). The first of them suggests that sea organisms had more space to peak in the early Late Ordovician, and the second hypothesis suggests that such a space was comparable in the analyzed time slices. Such a result is very interesting, because it matches better the "classical" biodiversity curves (Purdy 2008; Aberhan & Kiessling 2012; Aberhan *et al.* 2012; based on the data from Sepkoski 2002) than the "innovative" curve proposed by Alroy *et al.* (2008). One should note that the former curve indicates that the late Early Devonian peak was just a bit smaller than that early Late Ordovician (Fig. 1).

Of course, all considerations presented above are highly hypothetical, and it would be wrong to say that they are enough to support one of the alternative marine biodiversity curves. For instance, we do not know what was the relative importance of the discussed constraints of space-biodiversity links. It cannot be excluded that, say, the pole-to-equator differentiation was more important than the connectivity of shelfal environments, and so on. Moreover, the available plate tectonic, palaeoclimatic, and eustatic reconstructions still need serious improvement. However, the attempted qualitative analysis provides some important ideas for further discussions.

Conclusions

The qualitative analysis of the available information on the global Late Ordovician and Early Devonian plate tectonics, palaeoclimate, and sea level and the attempt to imply its results for judgements about the alternative biodiversity curves allow two main conclusions:

– apparently, global shelfal environments shrank, concentrated in the tropics, and were better connected in the late Early Devonian relatively to the early Late Ordovician;

– hypothetically, there was more (or the same) space for marine biodiversity to peak in the early Late Ordovician than in the late Early Devonian, which matches better the "classical" biodiversity curve.

Testing these too tentative ideas quantitatively appears to be an important task for further studies. However, quantification of the area of Late Ordovician and Early Devonian shelves is challenging because of two reasons. On one hand, the available global palaeogeographical reconstructions (e.g., that by R.C. Blackey - see on-line at ww2.nau.edu/rcb7/globaltext2.html) differ is some what from some other global plate tectonic reconstructions (e.g., Stampfli & Borel 2002; von Raumer & Stampfli 2008; Wilhem *et al.* 2012; Stampfli *et al.* 2013). On the other hand, the above-mentioned global plate tectonic reconstructions depict only tectonic blocks, not palaeoshorelines, and, thus, they cannot be employed directly for precise delineation of ancient shelves. The reconstruction proposed by Cocks & Torsvik (2013) is an exception (both tectonic blocks and palaeoshorelines are indicated there), but it embraces the only portion of the planetary space. Moreover, the summarized area of shelves around small oceanic islands (that are difficult to consider on the modern reconstructions) should not be ignored. And yet another caution is reasonable. As shown by Peters (2007), elongated shelves around land masses and widespread shelves of epeiric seas (better to say, such seas embraced only shelves) might have been different habitats. If so, further studies should differentiate palaeoenvironments, which are judged together as “shelfal” in this paper.

Of course, the size and the palaeogeographical distribution of shelves were not the only possible controls on the biodiversity. Many other forces, both extrinsic (i.e., environmental) and intrinsic (i.e., biological), as well as their interconnections should be considered – e.g., the content of the atmospheric oxygen (Berner 2006) and/or the perturbations in the sulphur isotopic record (Hannisdal 2011). Or, if there were teleconnections between marine and non-marine environments / ecosystems in the Late Devonian (Algeo *et al.* 1995), the rise and the dispersal of terrestrial floras in the Early Devonian (Niklas *et al.* 1983; Meyen 1987; Anderson *et al.* 1999) might have been also significant factor influencing the marine biodiversity. Finally, it would be wrong to forget that reaching the peak in the number of taxa depended on the geologic time itself, i.e., on the duration of the radiation, and the rate of global biotic evolution.

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Резиме

Да ли је за максимум морског биодиверзитета било више простора у горњем делу доњег девона него у доњем делу горњег ордовицијума? – кратак осврт

После тзв.”камбријумске експлозије“, морски биодиверзитет достиже свој максимум или у доњем делу горњег ордовицијума или у горњем делу доњег девона.Тешко је коментарисати неслагања која постоје око две криве биодиверзитета, мада би расправа могла бити започета са проценом услова који су погодовали развоју морског биодиверзитета у доњем делу горњег ордовицијума као и у горњем делу доњег девона. Највероватније су везе које су постојале између различитих делова мора и океана омогућиле развој и разноврсност морских организама одређених региона. У највећем броју случајева шелф се издваја као средина која је нарочито повољна за развој организмима и која је омогућила њихову велику бројност и разноврсност. Палеосредине које су имале широко распрострањене у доњем делу горњег ордовицијума као и у горњем делу доњег девона, поређене су на основу њихове релативне величине, распрострањења у односу на екватор и полове, као и њихове повезаности са шелфом. Постојећа реконструкција тектонских плоча указује да је фрагментарност континенталних маса током доњем делу горњег ордовицијума и горњем делу доњег девона, мање или више слична, као и да је степен ове фрагментараности био умерен. Такође би могло да се претпостави да је нагиб континенталних падина, који је често тектонски контролисан, био приближно сличан и то у глобалним размерама током ова два временска раздобља. Стога, успостављена фрагментација копнених маса као и нагиб континенталне падине указују на сличне величине шелфних средина у проучаваним раздобљима. Утврђена је значајна разлика у односу на ниво светских мора који је био трећи фактор који је утицао на величину шелфова, а који био 1,5 пута нижи у горњем делу доњег девона него у доњем делу горњег ордовицијума. Ово указује на то да су шелфне средине током овог последњег временског периода вероватно биле значајно веће. Уопштено говорећи, поменути временски периоди, чије је упоређење извршено, карактеришу се углавном сличним климатским условима, с тим што су за сваки од њих постојале и одређене специфичности везане за климу у областима полова и екватора. У горњем делу доњег девона долази до повећања концентрације шелфних средина у тропским областима, веће повезаности између шелфова, као и већег кретање тектонских плоча, него у доњем делу горњег ордовицијума. Претпоставка је да је било више (или исто) простора за достизање максимума у развоју морског биодиверзитета у доњем делу горњег ордовицијума него у горњем делу доњег девона, што се поклапа са ”класичном“ кривом биодиверзитета. Провера ове две идеје квантитативно представља важан задатак за будуће студије. Наравно, величина и палеогеографско распрострањење шелфова нису само могуће контроле биодиверзитета. Многи други фактори, како спољашњи (тј. животна средина) тако и унутрашњи (тј. биолошки), као и њихова међусобна повезаност мора бити разматрана. Најзад, било би погрешно запоставити да достигнути максимуми у броју таксона зависе од геолошког старости, тј. трајања радијације и степена глобалне биотске еволуције.

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Middle Miocene Badenian transgression: new evidences from the Vrdnik Coal Basin (Fruška Gora Mt., northern Serbia)

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Abstract. The latest field investigation of the Vrdnik Coal Basin as well as new data from numerous boreholes enabled the finding of an unconformity between the undivided continental-lacustrine Lower Miocene and the marine Middle Miocene Badenian. The different terrestrial-lacustrine sediments indicate a very mobile and dynamic environment (according to known drilling data, the total thickness of these deposits reaches up to 300 m). All these rocks belong to the Vrdnik series (Vrdnik Formation). The evolution of the Vrdnik series is distinguished by several stages (*e.g.* pre-lacustrine, lacustrine, peat-swamp, *etc*.). Each of these phases was proved by their sedimentologic and structural characteristics. On the other hand, among the fossils, only the swamp flora remains (*Sequoia, Laurus, Taxodium, Glyptostrobus, etc.*) and poor and fragmented ostracode valves (*Candona* sp.) were documented. Presently, the exact stratigraphic position of the Vrdnik series is unknown. Discordantly over the mentioned rocks, real marine sediments of the Paratethys Sea occur. To date, it was a completely unknown subsurface distribution of these sediments. Among a few types of rocks that have a small distribution, the so-called the Leitha limestones (Middle Miocene, Badenian) have great significance (up to 98% of $CaCO_3$). The total thickness of the limestones reaches up to 70 meters (borehole B-11). The findings of key foraminifer species (*Orbulina – Globigerinoides* Zone) indicate an early Badenian (Moravian) transgressive event (*ca*. 15 Ma). Lithologically, it is represented by gray, sandy marls and sandy clays, coarse-grained sands and microconglomerates in the base of the mentioned limestones (boreholes B-11, B-15, B-19, and B-21) with a total thickness of up to 15 meters.

Key words: Middle Miocene Badenian, marine transgression, Vrdnik Coal Basin, northern Serbia.

Апстракт. Најновија теренска истраживања Врдничког угљеног басена, као и нови подаци из бројних бушотина, допринели су да се укаже на дискордантан и трансгресиван однос између нерашчлањеног континентално - језерског доњег миоцена и морског средњег миоцена, бадена. Различити копнени и језерски седименти указују на врло мобилну и динамичну палеосредину (према познатим бушотинским подацима, укупна дебљина ових наслага достиже и до 300 m). Све те стене заједно припадају Врдничкој серији (Врдничкој формацији). Настанак и развој Врдничке серије одвијао се кроз неколико фаза (нпр. пре - језерска, језерска, тресетно-мочварна, итд). Свака од ових фаза је доказана на основу одређених седиментолошких и структурних карактеристика. С друге стране, од фосила једино су запажени остаци мочварне вегетације (*Sequoia, Laurus, Taxodium, Glyptostrobus*, итд) и ретки, фрагментирани капци остракода (*Candona* sp.). Због тога, тачно стратиграфско место Врдничке серије није познато. Дискордантно преко поменутих стена наталожени су прави морски седименти Паратетиса. До данас, било је потпуно непознато потповршинско распрострањење ових седимената. Међу неколико типова стена које имају мало распрострањење, тзв. лајтовачки кречњаци (средњи миоцен, баден) имају велики значај (имају до 98 % $CaCO_3$). Укупна дебљина кречњака достиже и до 70 метара (бушотина Б-11). Налазак руководећих фораминиферских врста *Orbulina – Globigerinoides* зоне, указује на старије баденски (моравиан) трансгресивни догађај (преко око 15 милиона година). Литолошки, ова зона је представљена сивим, песковитим лапорцима, песковитим глинама, грубозрним песковима и микроконгломератима који се налазе у бази поменутих кречњакаа (бушотине Б-11, Б-15, Б-19 и Б-21) и њена укупна дебљина достиже и до 15 метара.

Кључне речи: Средњи миоцен, баден, морска трансгресија, Врднички угљени басен, северна Србија.

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Introduction

During the Upper Oligocene and early Lower Miocene, young Alpine tectonics (so-called the Sava phase) created conditions for the development of continental–lacustrine sediments in a large area along the southern margin of the Pannonian Basin and within the Dinaride Lake System (KRSTIĆ *et al.* 2003, 2012; MANDIC *et al.* 2012; DE LEEUW *et al.* 2012). This more or less similar sedimentation regime lasted more than eight million years in the southern Pannonian domain (*ca.* 23–15 Ma). During the late Lower Miocene, subsidence and sedimentation were effects of the syn-rift extension phase that resulted in the formation of numerous grabens filled by thin syn-rift marine deposits (HORVÁTH *et al.*, 2006). The Middle Miocene Badenian transgression is one of the most important events that occured within the Miocene. It left observable marks over the whole Central Paratethys, especially in the Pannonian Basin (ĆORIĆ & RÖGL 2004; ĆORIĆ *et al.* 2004, 2009; LATAL *et al.* 2006; KOVAČ *et al.* 2007; UTESCHER *et al.* 2007; HARZHAUSER & PILLER 2007; PILLER *et al.* 2007; HARZHAUSER *et al.* 2003, 2011; HOHENEGGER *et al.* 2009; MANDIC *et al.* 2012). A lot of evidence pointing to a sudden change in the sedimentation regime was described on the southern margin of the Pannonian Basin especially (BAKRAČ *et al.* 2010; KRSTIĆ *et al.* 2012; PEZELJ *et al.* 2013; TOLJIĆ *et al.* 2013). The event was tentatively synchronous and occurred at the beginning of Badenian age but, in fact, it was at different times affecting a large area of Paratethys (*ca.* 15 Ma). In Serbia, almost as a rule, different Badenian marine sediments unconformably and transgressively overlie the colorful series of the Lower Miocene clastics (ČIČULIĆ 1958; DOLIĆ 1961, 1998; ČIČULIĆ-TRIFUNOVIĆ & RAKIĆ 1977; PETKOVIĆ *et al.* 1976; MAROVIĆ *et al.*, 2007; RUNDIĆ *et al.*, 2005, 2011, 2013, 2013a). All the mentioned authors noted the minor occurrence of the Middle Miocene at the southern flank of the mountain. An exception was the Vrdnik Coal Basin, where sediments of the Lower Miocene transgressively overlie the basement rocks (PETKOVIĆ *et al.* 1976). There are no other significant occurrences of Miocene rocks at the southern slope of the Fruška Gora Mt. Herein, for the first time, a significant subsurface distribution of the Middle Miocene rocks is shown.

This paper presents new stratigraphic and paleontological data from the Vrdnik Coal Basin, the largest Lower Miocene area on the southern slope of the Fruška Gora Mt. (Fig. 1). The studied area had had a long mining history (since 1804). However, after the last spectacular ground water flooding (1968), all the exploitation works were ceased forever. Soon afterwards, the mining activity was replaced by tourism and recently, it has become a very popular spa destination in Serbia.

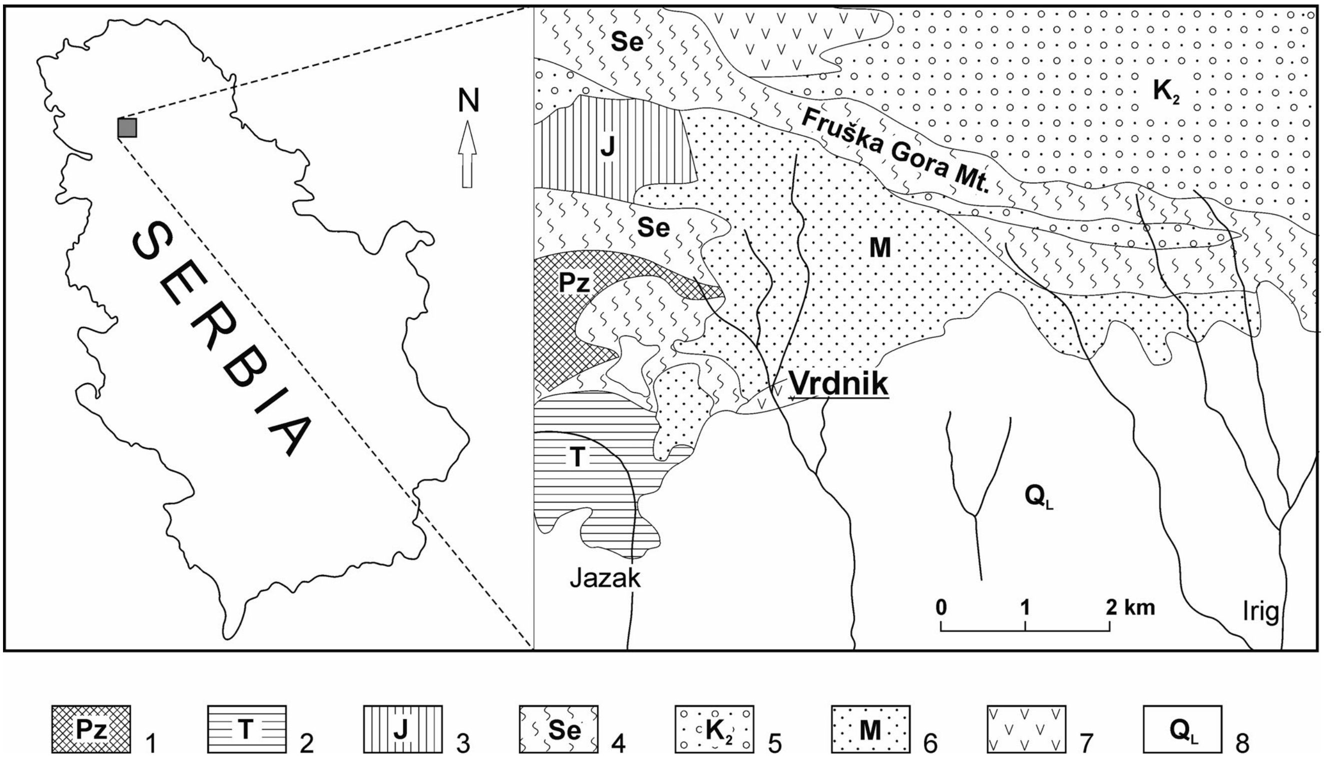


Fig. 1. Geographic position and the simplified geological map of the southern slope of Fruška Gora Mt. Key: **1,** Paleozoic; **2,** Triassic; **3,** Jurassic; **4,** Serpentinites; **5,** Upper Cretaceous; **6,** Miocene (general); **7,** Miocene volcanites; **8,** Quaternary (Loess).

A short review of the geology of the Vrdnik Coal Basin

The Vrdnik Coal Basin (VB) represents a relatively narrow, tectonic subsided structure between the Fruška Gora Mt. and Vrdnik where Miocene deposits occur along a discontinuous belt with E–W direction. Within the VB, Lower Miocene continental–lacustrine sediments, known as the Vrdnik Series (= Vrdnik Formation (VF)), represents the oldest Neogene unit (PETKOVIĆ *et al.* 1976; ČIČULIĆ & RAKIĆ 1976; RUNDIĆ *et al.* 2011, 2013). It discordantly overlies a Pre-Tertiary paleorelief (Triassic alevrolites and dolomitic limestones, serpentinites, Jurassic meta-sediments, Upper Cretaceous sandstones, *etc*., see Fig. 1) and is covered by Middle-Upper Miocene sediments at the higher parts of the mountain. Lithologically, these deposits consist of heterogeneous clastites (varicolored gravelly clay, gravel, sand, and conglomerate). On the northern slope of the Fruška Gora Mt., the VF discordantly overlies the various members of older, pre-Neogene units (ČIČULIĆ & RAKIĆ, 1976). In certain places, the contact with the older formations is tectonic (*e.g.* VF/serpentinites). The VF is better developed and studied on the southern slope of the Fruška Gora Mt. (environs of the Vrdnik spa especially), where deposits of brown coal and well-known fossil flora sites are situated. The Upper Oligocene (KOCH 1876) or Lower Miocene (PANTIĆ 1956) age of these rocks were considered. Based on their superposition, three litho-stratigraphic members are distinguished among them: 1) at the base, various breccia, conglomerate, and sandstone are present, 5–30 m thick; 2) above that, there is a coal–bearing horizon. It is composed of 4–6 coal layers, 0.6–2.5 m thick, represented by intercalated layers of montmorionite clay (bentonite, up to 1m thick); 3) the overburden of the coal layer is composed of lower and upper overburdens. In the lower overburden of the coal layers, there is some bituminous marl and clay, 10–12 m thick, containing remains of fossil flora, which is according to PANTIĆ (1956) dominated by the species: *Taxodium distichum*, *Glyptostrobus europeus*, *Sequoia langsdorfi*, *Castanea atavia*, *Quercus drimeja*, *Myrica lignitum*, *Zelkova ungeri*, *Laurus princes*, *Leguminosites gondini*, *etc*. In addition, the palynological analyses indicate the Lower Miocene age of these sediments. In the upper overburden of the coal horizon, there is a package of diverse sandstones, multicolored clays, sands, and rarely tuff. The layers of the upper overburden are characterized by greater thickness, which may be over 100 m. Based on earlier data from boreholes, the whole thickness of the VF is more than 250 m (PETKOVIĆ *et al.* 1976). However, the latest unofficial data from some boreholes in the area of the Vrdnik spa suggest a much greater thickness of the mentioned rocks. Recently, a similar observation was reported (RUNDIĆ *et al.* 2013a; TOLJIĆ *et al.* 2013).

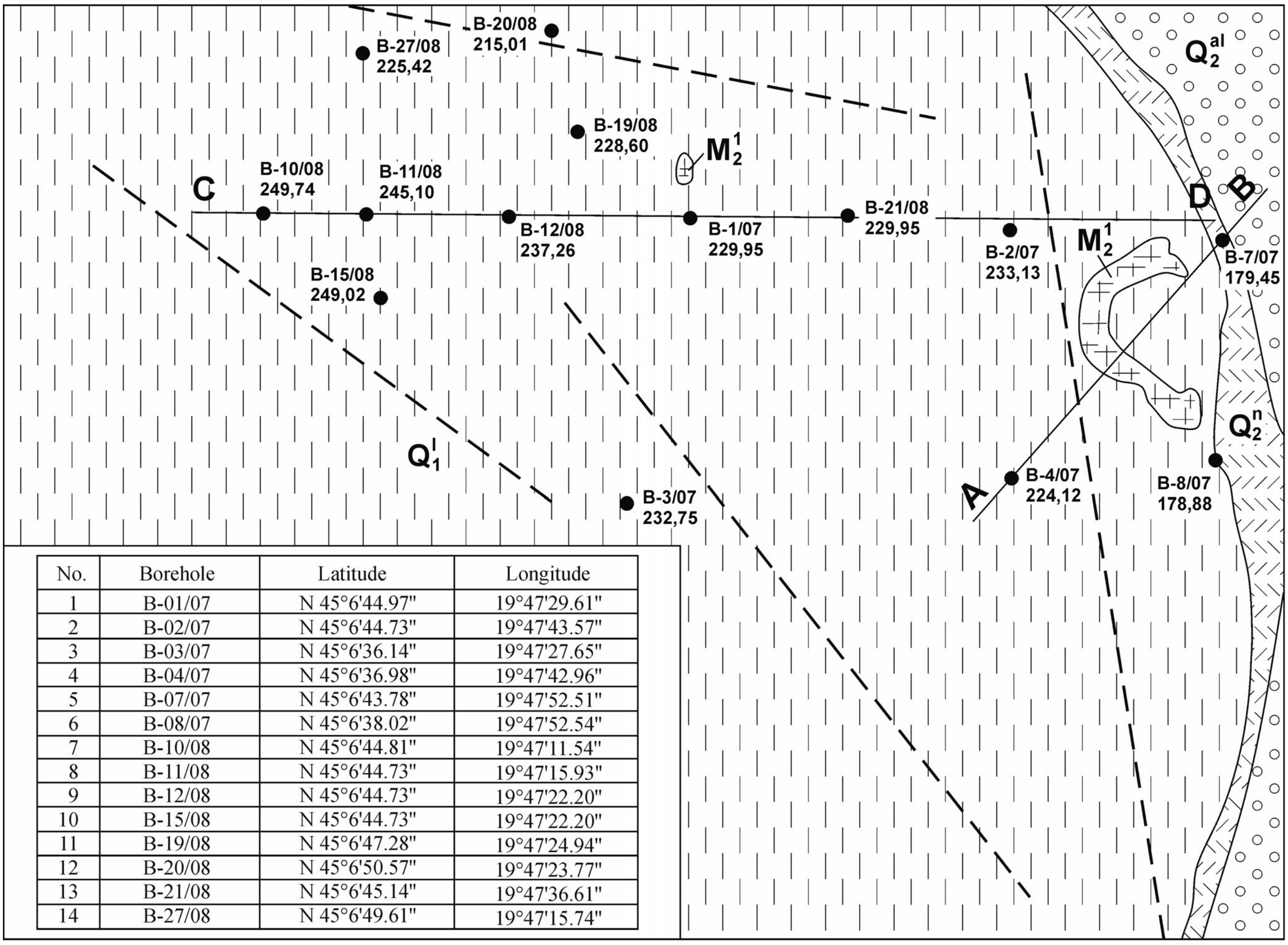
According to earlier data from the basic geological map, sheet Novi Sad, 1:100 000, the mentioned deposits lie below various Middle Miocene Badenian sands, conglomerates, sandy marls and clays, and different limestones and sandstones (ČIČULIĆ & RAKIĆ 1976). On the surface, marine Badenian deposits located at several places to the south of the Vrdnik spa have a very small distribution. On the other hand, their, to date, unknown subsurface spreading is very significant and their determination represents the main goal of this paper. Herein, the marine sedimentation was interrupted at the end of Badenian time and the deposition break lasted until the Upper Miocene. It was connected to the well-known marine regression at the beginning of the late Middle Miocene. Subsequently, a very small lacustrine phase during the Pannonian age (Lake Pannon) affected this area and resulted in the deposition of the so-called Beočin marls (RUNDIĆ & POTIĆ 2013). During the latest Middle Miocene, Pliocene, and Quaternary, because of the uplifting of the Fruška Gora Mt., different terrestrial sediments were formed (freshwater equivalents of the Upper Miocene –Pontian, the Pleistocene Srem series, the loess-paleosoil sequences, *etc*).

Materials and Methods

All the presented data were obtained from field investigations (2010, 2011) and from core-samples of twenty-seven boreholes drilled during 2007 and 2008. Many data were collected and more than a half of these boreholes are presented herein (Fig. 2). All the measured logs were performed in the field. Later, the logs were compared and more precise stratigraphic analyses were realized (Figs. 3–6). Different and relatively abundant marine fauna (mollusks, foraminifers, ostracodes, echinoids, corals, etc.) from forty core-samples were determined. Ten limestone samples were examined by thin-sections. Additionally, the four soft samples from the boreholes B-19 and B-20 were treated with 6 % hydrogen peroxide and later washed (0.5–0.063 mm sieves). Approximately 100 g of each dried residue was examined under a stereomicroscope. All the mentioned material is stored at the Hidro-Geo Rad Co., Belgrade and at the Chair of Historical Geology, Faculty of Mining and Geology, University of Belgrade. Some information was plotted on a geodetic plan on the scale 1:2500, and two simplified geological cross-sections were drawn (Figs. 10, 11).

Results

Quaternary deposits, mainly loess-paleosoil sequences, cover the area of the southern and southwestern part of the Vrdnik Coal Basin. The subsurface investigation of the wider area of Strmoglavnice and Velika



No.	Borehole	Latitude	Longitude
1	B-01/07	N 45°6'44.97"	19°47'29.61"
2	B-02/07	N 45°6'44.73"	19°47'43.57"
3	B-03/07	N 45°6'36.14"	19°47'27.65"
4	B-04/07	N 45°6'36.98"	19°47'42.96"
5	B-07/07	N 45°6'43.78"	19°47'52.51"
6	B-08/07	N 45°6'38.02"	19°47'52.54"
7	B-10/08	N 45°6'44.81"	19°47'11.54"
8	B-11/08	N 45°6'44.73"	19°47'15.93"
9	B-12/08	N 45°6'44.73"	19°47'22.20"
10	B-15/08	N 45°6'44.73"	19°47'22.20"
11	B-19/08	N 45°6'47.28"	19°47'24.94"
12	B-20/08	N 45°6'50.57"	19°47'23.77"
13	B-21/08	N 45°6'45.14"	19°47'36.61"
14	B-27/08	N 45°6'49.61"	19°47'15.74"

Fig. 2. A geological map of the investigated area and the positions of the boreholes (black circles and WGS84 coordinates), and the location of the geological cross-sections (A–B, C–D).

Pećina determined the geological structure and provided many previously unknown data. According to the BGM, sheet Novi Sad 1:100,000 (ČIČULIĆ-TRIFUNOVIĆ & RAKIĆ 1977), on the surface were only a few small "patches" of marine Badenian sediments. They transgressively overlaid Lower Miocene freshwater deposits. On surface of the studied area, regardless of the package of quite thick Quaternary sediments, smaller outcrops of multicolored, gray-bluish, brown and reddish clay, and brown ferruginous sands (Fig. 3 A, B). They represent the final part of the lithological succession of the VF. A part of the continental-lacustrine series was discovered in some of the boreholes (*e.g.*, B-19 (72.80–76.90 m), B-20 (20.70–36.60 m), and B-27 (17.50–32.00 m – see Figs. 3C, 8). Generally, it consists of green, bentonite clays, and carbonaceous clay without fossil remains. Moreover, in almost all the other exploration wells, Middle Miocene Badenian deposits were registered. They overlie the Early Miocene clays and indicate the marine transgression in this area (Figs. 4–8).

The marine Badenian sediments have a relatively small distribution in the Vrdnik Coal Basin and they include only a few different facies. If compared with the synchronous rocks on the northern parts of the mountain, a clear difference is evident (PETKOVIĆ *et al.* 1976; RUNDIĆ *et al.* 2011). However, Badenian limestones appear much more than all the other synchronous rocks. Generally, these sediments are present as a split rock body with E–W direction. According to borehole data, there are sporadic occurrences of very rare grayish-green clays and sandy marls and wider distribution of biogenic limestones (the so-called Leitha limestone, in all the other boreholes). They contain abundant fossils and these limestones could be distinguished as separate biofacies (*e.g.*, the Lithotamnian, Amphistegin, Bryozoan, *etc.*). The limestone is massive, reefy, developed by the activities of corallinacean red algae, foraminifers and bryozoans, *etc.* In addition, it includes various fossil remains of mollusks, echinoids, corals and other organisms. Based on sediment analyses, a dominance of algal and algal-foraminifer biomicsparite and biomicrudite was determined (Fig. 9). Laterally, toward the E–NE margin of the Vrdnik Coal Basin, the limestones turn into marly limestones, sandy marls and clays. Biostrati-

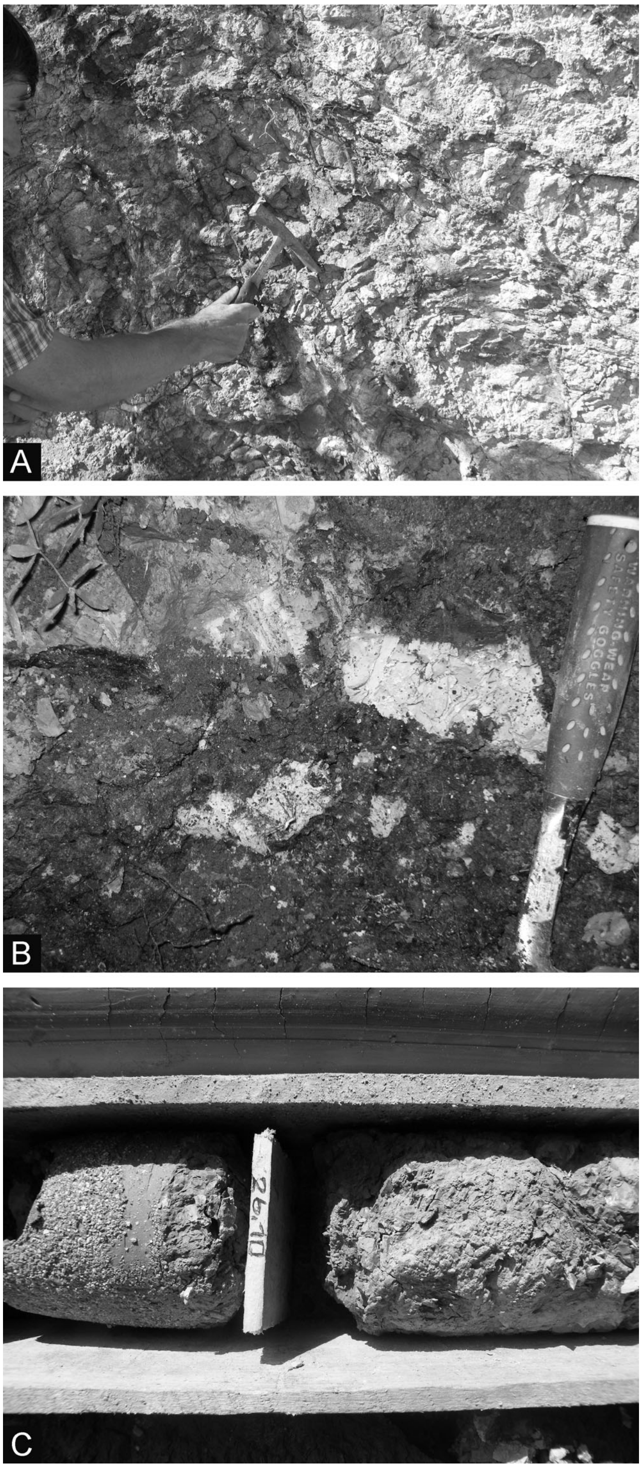


Fig. 3. The Lower Miocene Vrdnik series: **A, B,** Surface outcrops and **C,** A detail of green bentonite clay from the borehole B-20/08 (26.10 m).

graphically, the sediments of the Lower, Middle and Upper Badenian could be separated. Grayish sandy marls represent the oldest marine Badenian sediments. Occasionally, the Badenian sediments were overlaid by Upper Miocene (?Pontian) clastites or different Quaternary sediments (boreholes B-1, B-2, B-3 B-4, *etc*).

For example, in the borehole B-1/07 (N 45°6'44.97"; E 19°47'29.61" – Fig. 4) under different Pleistocene sediments and thin interbeds of ?Pontian gray alevrites (the first 17 meters of the core section), there is a relatively thick series of Badenian limestone (17.70–74.80 m). At higher levels, the limestone is more whitish, massive and has typical structural characteristics such as those documented in other areas of the Fruška Gora Mt. It is the well-known Leitha limestone (name after the Leitha Mountains, Austria). A sample from a depth of 38.50 m has a system of ca-

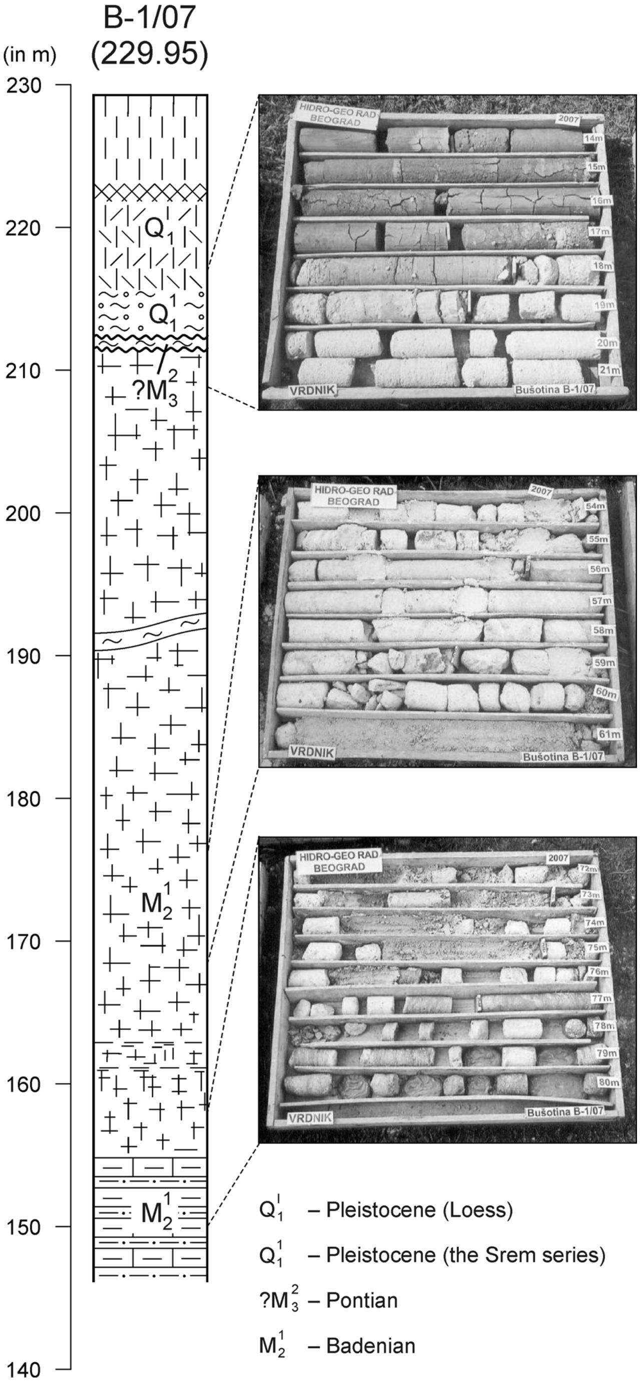


Fig. 4. The stratigraphic section and some core-samples from the borehole B-1/07.

verns, which are filled by reddish-brown alevrites and clays. This is a very common occurrence in these sediments (RUNDIĆ *et al.* 2011). These limestones alternate with gray and partly marly limestones in the deeper parts of the borehole (63.00–74.80 m). According to its structural properties and fossil association involved, it corresponds to the real bioclastic limestones (corallinaceans, bryozoans, foraminifers, echinoderms, bivalve remains, *etc.*). Although the red algae are not as dominant, the textural pattern is predominantly composed of unattached coralline algal branches, rhodoliths, and their detritus. FREIWALD *et al.* (1991) described a similar modern environment from Norway.

Based on the analyzes of thin-sections from core-samples, the facies comprises packstones, rudstones, and floatstones consisting of angular and subrounded corallinacean clasts. The corallinaceans are represented by *Lithothamnion, Mesophyllum*, and ?*Lithophyllum*. Sporadically, rhodoliths of corallinacean red algae are present (Fig. 9). Bivalves and gastropods occur in variable quantities (*Ostrea* sp., *Aequipecten* sp., and *Conus* sp.), as well as regular and irregular echinoids and bryozoans (64.50–65.00 m) which are represented by branching forms. Elsewhere, rotaliids forms, such as Amphistegina and ?Planostegina (37.00–37.50 m), scarce cibicidoids and miliolids represent the abundant foraminifers. In the deepest core interval (74.80–83.50 m), this bioclastic limestone is more fine-grained and alternates to sandy marl. From time to time, the genus Amphistegina has mass occurrence and can then make a separate biofacies – Amphistegina limestone (Fig. 9).

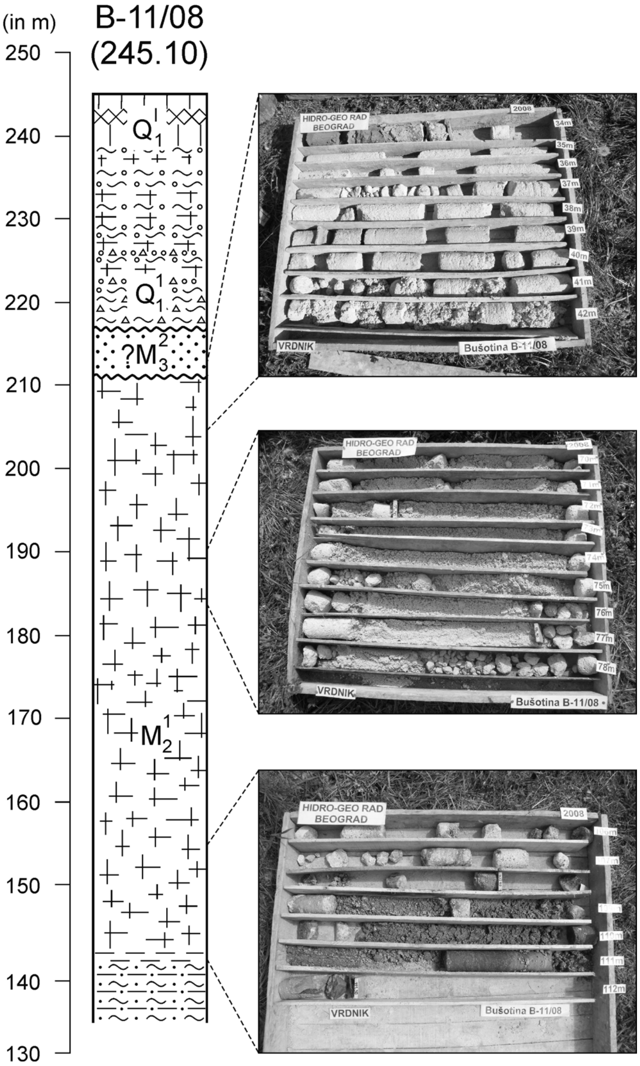


Fig. 5. The stratigraphic section and some core-samples from the borehole B-11/08. For key, see Fig. 4.

In the borehole B-11/08 (N 45°6’44.73”, E 19°47’15.93” – Figs. 5, 11), under a thicker package of ?Pontian and Quaternary sediments (total thickness of approximately 33.50 m), two different facies of Middle Miocene Badenian were determined (RUNDIĆ *et al.* 2013a). Leitha bioclastic limestone with a very diverse fauna of corallinacean algae, bryozoa, foraminifers, mollusks, and echinoderms was determined at depth of 33.50–104.00 m. In all the boreholes in this area, it is the thickest package of limestones that has been specified (thickness almost 70 m). The limestones are not the same everywhere; there are few differences in texture, fossils and color (whitish to light yellow in shallow samples, and more grayish in the deeper samples of the borehole (80.50–104.00 m). In the sample from depth of 35.00–35.80 m, foraminifer species *Amphistegina mammilla* is dominate, while elphidiums and rotalids are individually present. Besides corallinacean algae and bryozoa that are macroscopically observable, very numerous bivalves were found in a sample from a depth of 82.50–83.00 m (Fig. 6): *Glycymeris pilosus, Flabellipecten besseri,* ?*Gigantopecten sp., Chlamys latissima, Cardiocardita partschi, Panopea menardi,* and *Ostrea* sp.(cf. *Ostrea lamellosa*), and significantly less gastropods (*Conus* sp. and *Turritella* sp.). In the gray, sandy limestone (87.50–88.00 m) algal and bryozoans sections dominated (Fig. 9). The algal-zoogenic biomicrudite/floatstone is real. Within the rock, algal and zoogenic fragments are visible (> 2 mm). The deepest sample (109.5–110.00 m) taken from gray, sandy, and sandy-marl clay represented a completely different facies of the Badenian Stage. Based on fossil associations with the predominant forms of planktonic foraminifera (*Orbulina suturalis*, *Globigerinoides* cf. *trilobus*, and *Uvigerin*a sp.) and mollusks such as *Ammusium cristatum* and *Dentalium* sp., and other smaller forms of bivalves, it could be assumed that these sediments belong to the Lower Badenian Lagenidae Zone. At moment, the precise biostratigraphic position of these layers (?Lower or Upper Lagenidae Zone) is unknown and requires detailed quantitative and qualitative analyses of the mentioned foraminifers and calcareous nannoplankton (ĆORIĆ *et al.* 2009; HOHENEGGER *et al.* 2009; PEZELJ *et al.* 2013) as well

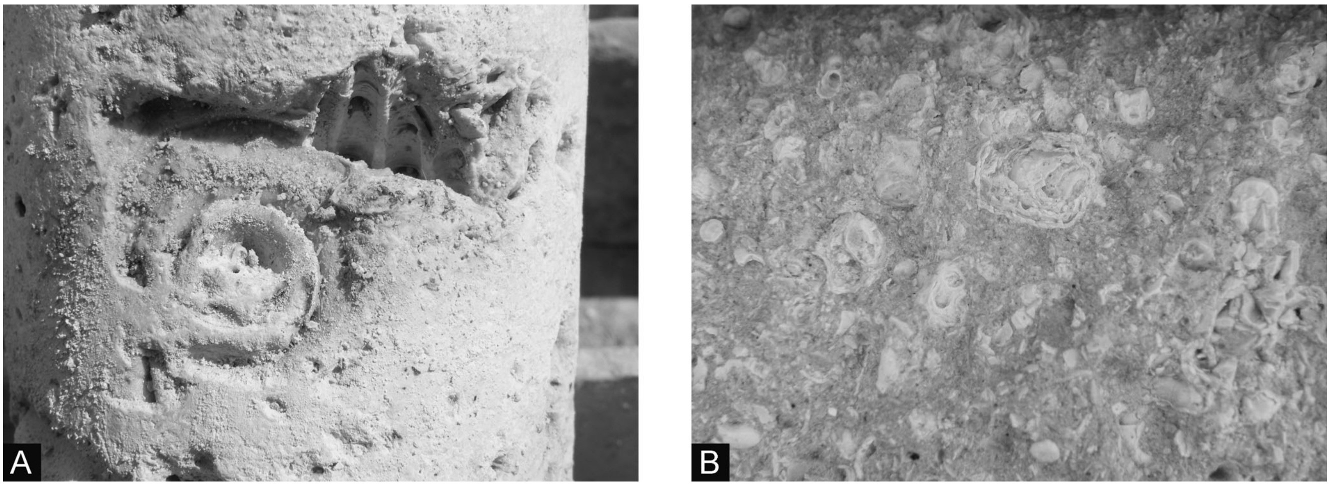


Fig. 6. The bioclastic limestone: **A,** Remains of bivalves (? *Chlamys* sp.) and gastropods (*Conus* sp.) from the borehole B-11/08 (82.50–83.00 m), and **B,** the core sample with rhodoliths – corallinacean limestone (B-12/08, 79.20 m).

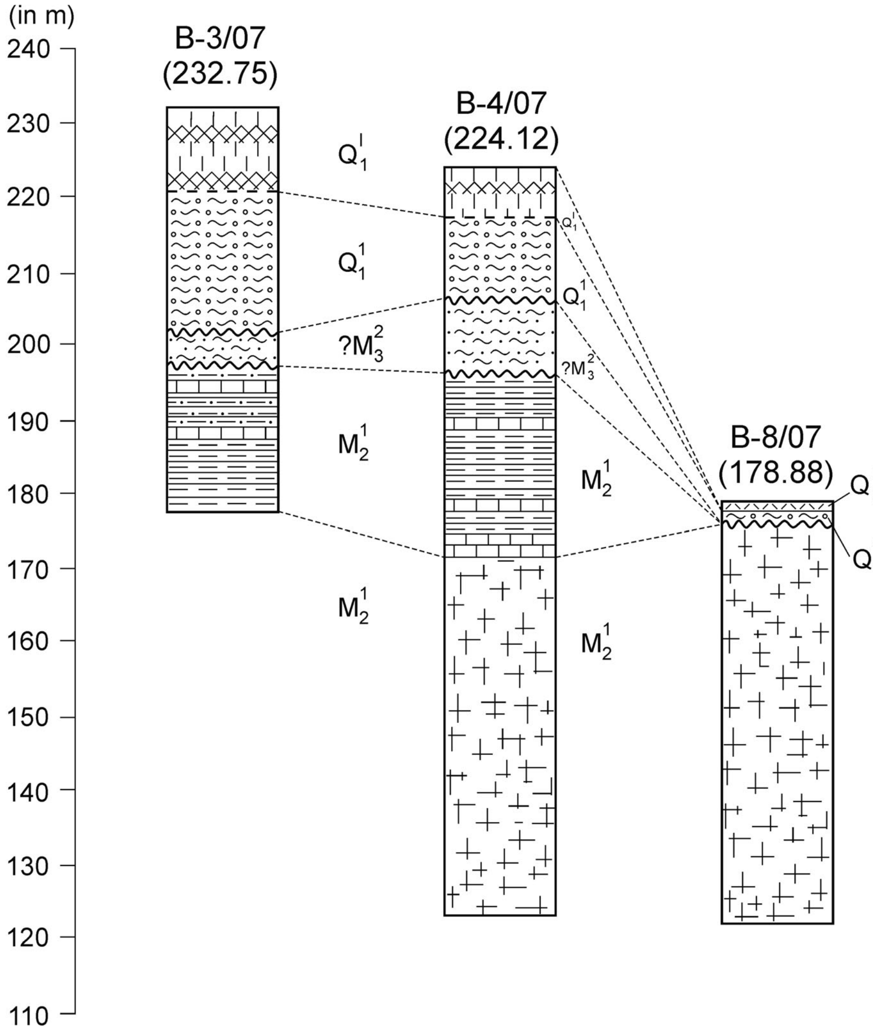


Fig. 7. Comparative stratigraphic logs of boreholes B-3/07. B-4/07, and B-8/07.

as provision of the initial time of marine flooding in this area (Mandic *et al.* 2012).

In the other boreholes, the lithological pattern is similar (Figs. 7, 8). The Badenian deposits are largely presented by bioclastic limestones (B-2/07, B-3/07, B-4/07, B-7/07, B-8/07, B-9/08, B-10 / 08, B-12/08, B-19/08, B-20/08, B-21/08 and B-27/08 – see Fig. 3). Exceptionally, other different facies of the Badenian stage were observed (*e.g.*, B-11/08, B-19/08). Lithologically, these are represented by sandy marls and sandy clays, coarse-grained sands, gravel and microconglomerates. The very scarce fossil remains (mostly planktonic foraminifers such as Globigerinoides and Orbulina) enable the oldest Badenian age to be suggested. In boreholes B-11/08, B-15/08, and B-19/08, these sediments make the basis of the mentioned bioclastic limestones. Sometimes, they consist of well-rounded but poorly sorted polymict gravel (1–5 cm) composed of metamorphic and carbonate rocks (Čičulić & Rakić 1976). They are supported by fine-grained quartz sand reaching 60–80% and occasionally clay up to 20 %. (Fig. 8, see B-19/08). Quartz fine-sand layers or dispersed fine-sand lenses of variable thickness (cm to dm) are intercalated within the

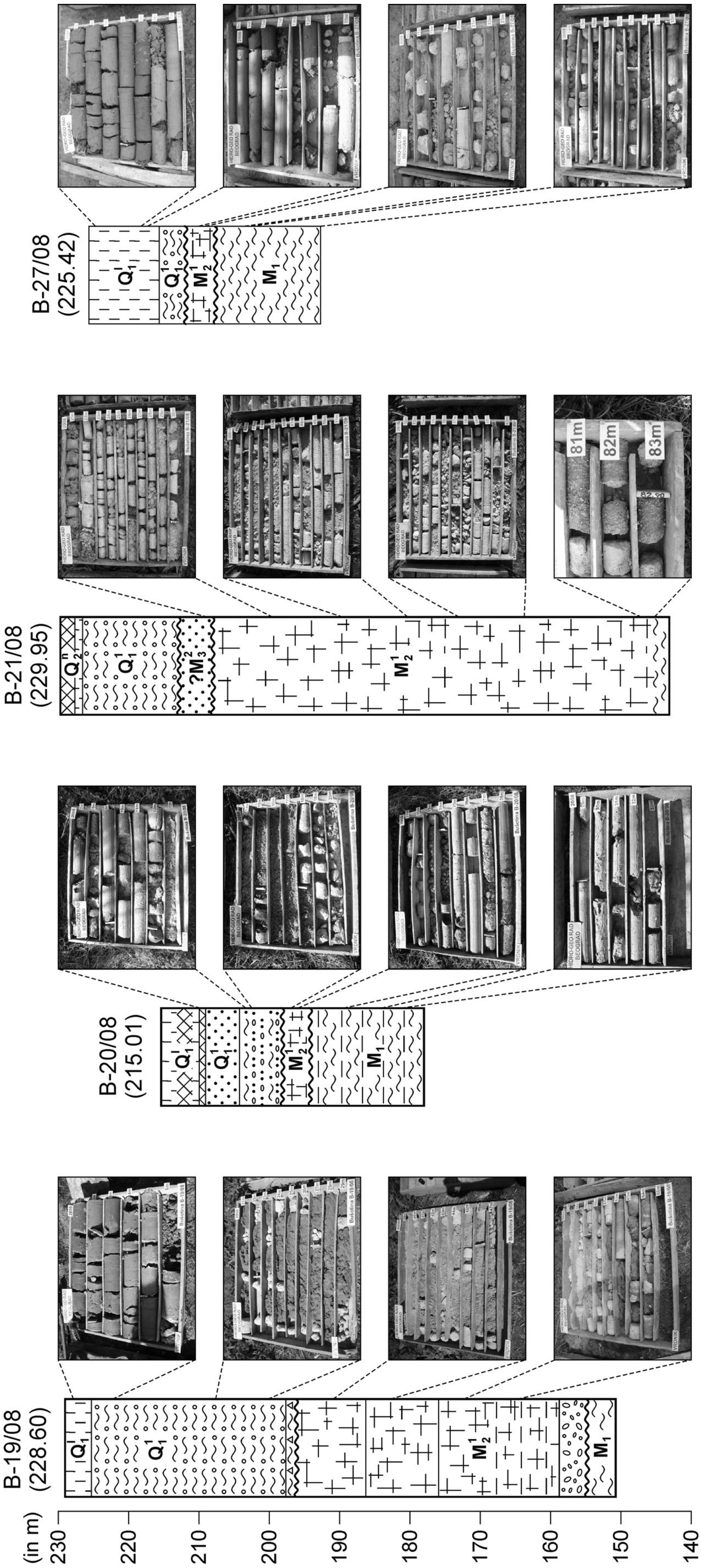


Fig. 8. Comparative stratigraphic logs of boreholes B-19/08. B-20/08, B-21/08 and B-27/08.

gravels. However, in the boreholes B-3/07 in the depth interval between 34.90–54.60 m and B-4/07 (28.00–50.50 m) very similar gray sandy marls overlie bioclastic limestones. They contain marine foraminifers and ostracodes (predominantly rotalids forms of foraminifers), which probably belong to the Upper Badenian age.

Discussion and interpretation

All the mentioned data derived from the borehole sections and surface outcrops clearly suggest a relatively wide subsurface distribution of the Middle Miocene marine sediments. More or less, these sediments represent a part of the well-known carbonate ramp, which was formed during the Middle Miocene (Langhian/Badenian) Climatic Optimum (SCHMID *et al.* 2001; BÖHME, M. 2003; HARZHAUSER & PILLER 2007; RÖGL *et al.* 2008). According to the first evaluation, the dominant reef limestone occupies a relatively narrow strip of the east-west direction with a total length of about 1,200 m. The potential width of the limestone reservoir is about 250 m. The most prevailing limestone components are coralline red algae but bryozoans and rare corals locally formed small patch reefs (RUNDIĆ *et al.* 2011). Except these, other marine facies occur but they have a minor distribution. Stratigraphically, all of these marine sediments transgressively overlie Pre-Tertiary units or undivided Lower Miocene continental sediments.

From the lithological point of view, the basal part of the marine Badenian succession was made of gravels and sandy gravels (borehole B-19/08), which originated from different older tectonic units (ČIČULIĆ 1958; DOLIĆ 1961, 1998; ČIČULIĆ-TRIFUNOVIĆ & RAKIĆ 1976, 1977; PETKOVIĆ *et al.* 1976; RUNDIĆ *et al.* 2013a). They are relatively poorly sorted but well-rounded with a medium fine-sand content. The medium/high degree of roundness indicates relatively long transport and/or following coastal reworking. The exact provenience of the gravels is still unclear; the source area could be the basement rocks of the Fruška Gora Mt. (PETKOVIĆ *et al.* 1976; RUNDIĆ *et al.* 2005, 2011). WIEDL *et al.* (2012) have discussed river transport but also marine reworking by coastal breakers in a deltaic system. However, the sporadically presence of the coarse-grained sediments, gravels and microconglomerates within only one of the investigated boreholes is insufficient for a more precise reconstruction.

During the Miocene time, the southern part of the Pannonian Basin (*i.e.* the Vrdnik Coal Basin) was strongly affected by the Alpine orogeny (PETKOVIĆ *et al.* 1976; KOVAČ *et al.* 2007; TOLJIĆ *et al.* 2013). The Middle Miocene Badenian was the peak of the Miocene carbonate production in the Central Paratethys (SCHMID *et al.* 2001; HARZHAUSER & PILLER 2007; RÖGL *et al.* 2008; BASSO *et al.* 2008; PEZELJ *et al.* 2013; WIEDL *et al.* 2012, 2013). The Middle Miocene Climatic Optimum (MCO) led to an extension of the tropical belt and favored the wide distribution of coral reefs throughout the Mediterranean and Central Paratethys during the Langhian age (BÖHME 2003; HARZHAUSER & PILLER 2007; BASSO *et al* 2008). Coral reefs are found along the Mediterranean and the Central Paratethys up to the southern Vienna and Transylvanian Basins (WIEDL *et al.* 2012). From this distribution pattern of the circum-Mediterranean region, a subdivision into two biogeographic areas during the Langhian time is possible (WIEDL *et al.* 2012). Coral reefs (*sensu strictu*) characterize the southern area. Its northern boundary could be drawn from the Aquitaine Basin to the Vienna and Transylvanian Basins (WIEDL *et al.* 2012, 2013). Further to the north, the coral occurrences are characterized by coral carpets/assemblages. In this context, the Leitha limestone, which is positioned at the edge of the coral reef belt, indicates the transition zone between coral reefs to non-reefal coral communities (WIEDL *et al.* 2013). The distribution of corals in the Central Paratethys is linked with the Middle Miocene Climatic Optimum, which supported the northward shift of tropical elements (HARZHAUSER *et al.* 2003, 2011; WIEDL *et al.* 2013).

In the southwestern part of the Vrdnik Coal Basin, within the Badenian shallow-water carbonates (the Leitha Limestone), a few (bio) facies types could be recognized according to the abundance of some biogenic characteristics (*e.g.* Amphistegina, Bryozoan, Lithothamnion, *etc)*. Similarly, recent sediments up to 40 m of water depth were reported by RASSER (2000) from the Mediterranean Sea and HALFAR *et al.* (2000, 2012) from the Gulf of California. Generally, the Amphistegin's limestone is the youngest biofacies and corresponds to the Upper Badenian mostly. Other biofacies have stratigraphic range the Middle–Upper Badenian.

The Amphistegina limestone (Amphistegina biofacies) is characterized by the very common occurrence of the foraminer genus Amphistegina (Fig. 9A). Recent Amphistegina inhabit the tropical to subtropical belt in shallow waters down to 70–80 m where they are primarily attached to macrophytes with high densities. Their presence implies a minimum water temperature of 17°C (WIEDL *et al.* 2012). In summary, the Amphistegina subfacies was formed in a shallow, sublittoral environment with a depth range of *ca.* 20–30 m between the bryozoan subfacies and the mollusc subfacies. A typical bivalve of this facies is the deep-burrowing *Panopea menardi.* Modern representatives of Panopea live in sandy and muddy substrates preferring shallow subtidal habitats down to 20 m, burrowing between 0.6 and 2 m deep into the sediment (WIEDL *et al.* 2012). Besides, during the MCO, the optimal conditions resulted in extraordinary growth rates of oysters (*Crassostrea gryphoides*). Marine waters during the MCO in Central Europe displayed a seasonal temperature range of *ca.* 9–11°C. The absolute water temperatures ranged from 17–19°C during cool seasons and up to 28°C in the warm seasons (HARZHAUSER *et al.* 2011). The findings of bivalve species (?*Gigantopecten* sp., *Chlamys latissima*, *Glycymeris* sp., *Cardites partschi*, *Panopea menardi*, and *Ostrea* sp. (cf. *Ostrea lamellosa*) could support this paleotemperature pattern. A similar facies is present in the Badenian corallinacean limestones of Bosnia and Herzegovina, Croatia and Austria (ĆORIĆ & RÖGL 2004; ĆORIĆ *et al.* 2004, 2009; HOHENEGGER *et al.* 2009; PEZELJ *et al.*, 2013). In addition, the other foraminifers that were found in the Badenian sediments indicate more or less similar conditions. Thus, the relatively scarce finding of *Globigerina* sp. as well a *Globigerinoides* sp. may indicate short-time climatic oscillations of cooler climate during the MCO, which could be characterized as fairly uniform for the Badenian climate of the Central Paratethys realm (BÖHME 2003; BÁLDI 2006; KOVÁČOVÁ *et al.* 2009; KOPECKA 2012; WIEDL *et al.* 2012, 2013).

Modern Rhodolith-dominated carbonate systems are known worldwide (BASSO 1998; BASSO *et al* 2008; HALFAR *et al.* 2012 and references therein). The rhodolith biofacies (Fig. 9A) is represented by coralline algal rudstones with packstone matrix comprising spheroidal thin-branched rhodoliths (up to 6 cm). It also contains foraminiferal macroids with diameters of 0.3–2 cm. Interspaces between the rhodoliths and macroids are filled with coralline algal debris. Foraminifers are represented by rotalids (*Amphistegina* and *Ammonia*), and rare miliolids (*Borelis* sp.). Bryozoans are rare and commonly encrusted by coralline algae. A relatively similar rhodolith biofacies from the Leitha Mountains, Austria was well-described (WIEDL *et al.* 2012). For the mentioned facies types, these authors indicated water depths of 10–20 m. Consequently, a similar water depth could be suggests for this subfacies in the southwestern part of the Vrdnik Coal Basin.

The Bryozoan biofacies is very similar to the algal facies and in some places contain a rich bivalve fauna. Modern analogues are found on the Apulian shelf (Italia) along the seashore between 10–30 m of water depth (WIEDL *et al.* 2013). In addition, the bryozoan subfacies is associated with the Amphistegina subfacies (Fig.9B). A similar bryozoan facies was reported from the Mannersdorf Quarry, Austria. Therein, the facies is overlain by a coral facies. The co-occurrence of coral and bryozoan-bearing assemblages was explained by differences in the productivity of surface waters (WIEDL *et al.* 2012, 2013).

The Mollusk biofacies is equivalent to the bioclastic algal-mollusk facies and to the branching algal facies (BASSO *et al.* 2008) with its diversified molluskan assemblage. The mollusk biofacies consist of rudstones and floatstones that are characterized by high amounts of various mollusks. ZUSCHIN & HOHENEGGER (1998) described comparable mollusk assemblages from the modern Red Sea (Egypt). There, Turritellids are widely distributed on soft and hard substrates, muddy sediments, and on the reef slope down to 40 m; Cerithiids show distinct habitat preferences and occur in water depths up to 40 m with common occurrences between 5 and 30 m. The genus Glycymeris was described from sands between coral patches in depth of ca. 10 m (ZUSCHIN & HOHENEGGER 1998). Glycymerids are also reported from present-day sand bottoms at 10–30 m depth from the Florida Keys (see WIEDL *et al.* 2012). The mollusk biofacies is often associated with the rhodolith biofacies. The mollusk biofacies probably represents a shallow tran-

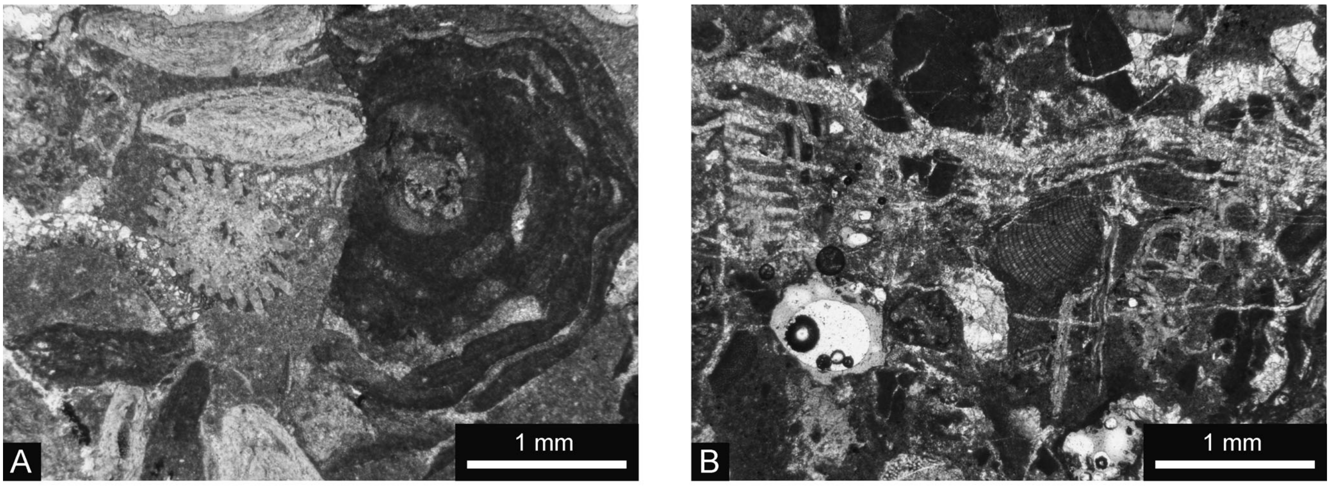


Fig. 9. **A,** Amphistegina biofacies with the rhodoliths, bryozoans and an echinoids section (B-1/07, 72.80–73.00 m); **B,** Algal-bryozoans biofacies (B-11/08, 87.50–88.00 m).

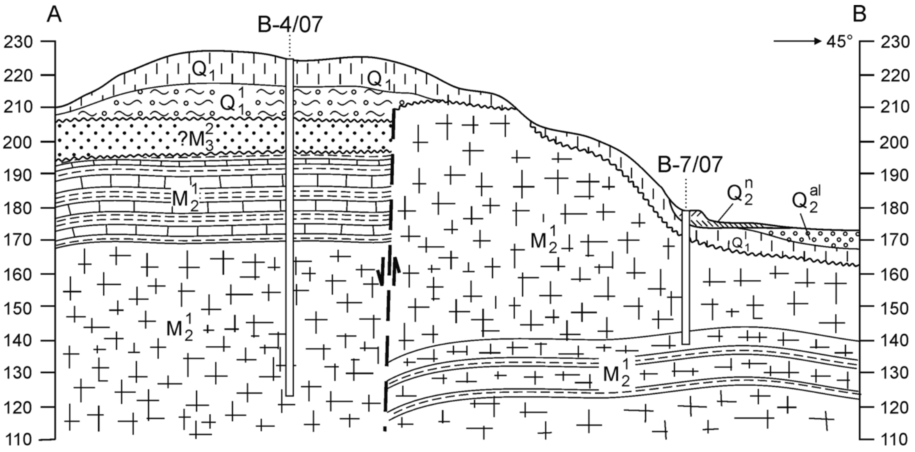


Fig. 10. A simplified geological cross-section (A–B) from the eastern part of the studied area.

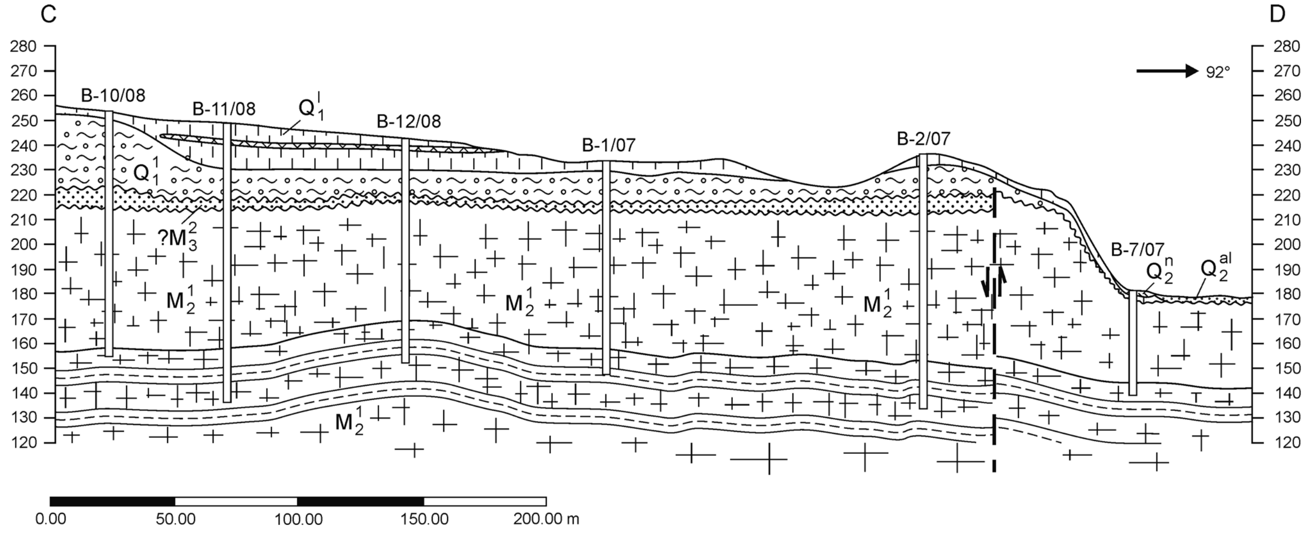


Fig. 11. A simplified geological cross-section (C–D) from the central part of the studied area.

sition zone between the rhodolith subfacies and relatively deeper water with the bryozoan biofacies.

Based on preliminary analyses of all the investigated boreholes as well as the surface distribution of the bioclastic limestones, the existence of the marine carbonate ramp in the southwestern part of the Vrdnik Coal Basin could be supposed. Additionally, an earlier study of similar sediments from the southern slope of the Fruška Gora Mt. (Rundić *et al.* 2011), indicated an elongated carbonate belt with E-W direction around the mountain (Fig. 11). The main part of it is yet undiscovered and our studies indicate to small, tectonically dislocated blocks. Based on the boreholes data, these carbonates underwent significant radial stress and were dislocated by fault tectonics after the Middle Miocene (Figs. 10, 11). This is in agreement with previously documented results from Bešenovo and Ležimir (more towards the west), where similar blocks of a shallow-water carbonate ramp occur (Rundić *et al.* 2011, 2013). In some places, they are displayed below different Quaternary sediments and they belong to small uplifted blocks where erosion processes were expressed (B-7/07, Fig. 10). On the other hands, there are relatively sunken blocks (B-4/07, Fig. 10) on whom, above the mentioned Badenian carbonates, much more younger stratigraphic units are present. A similar tectonic pattern was observed on the northern slope of the Fruška Gora Mt. (Čičulić-Trifunović & Rakić 1977; Petković *et al.* 1976; Rundić *et al.* 2005). However, therein there are no sedimentation breaks within the late Middle Miocene and there is a complete Neogene succession.

The studied boreholes showed subsurface features of Lower and Middle Miocene sediments, which were unknown before (presence/absence of stratigraphic units and their thickness, facial diversity, dip angle, unconformity, *etc.*). A preliminary analysis of fault structures in the Vrdnik Coal Basin is confirmed its complex structure and the character of a tectonic trench that was formed during the Miocene and inverted in the youngest stages of the Pliocene and Quaternary.

Conclusions

The data collected from surface researches and numerous boreholes in the southwestern part of the Vrdnik Coal Basin enabled the following conclusions:

- Based on lithological successions, stratigraphic logs and basic structural elements, the subsurface geological setting of the southwestern part of Vrdnik Coal Basin has been reconstructed. The following stratigraphic units were documented: the Lower Miocene, the Middle Miocene Badenian, the Upper Miocene ?Pontian, as well as different terrestrial sediments of Pleistocene age, including the loess-paleosoil sequences on surface.
- From a stratigraphic point of view, marine Badenian sediments transgressively and discordantly overlie older rock units (usually above the freshwater Lower Miocene Vrdnik series). They indicate the well-known regional transgression, which occurs in the Central Paratethys during the early Middle Miocene.
- There is a much larger subsurface distribution of Badenian sediments than previously supposed. Generally, they belong to an elongated carbonate belt that was generated during the Middle Miocene Climatic Optimum. Stratigraphically, this ?Upper Badenian carbonate ramp has a significantly wider distribution than a similar one formed during the Middle Badenian.
- Within the Badenian shallow-water carbonates, the so-called Leitha limestones have a dominant position and distribution (thickness over 70 m). They indicate a shallow reef environment (up to 40 m of water depth), relatively warm, clear water and favorable bionomical conditions nearby the Fruška Gora Island of the Central Paratethys. Among them, a few (bio) facies types could be recognized according to the abundance of some biogenic and textural characteristics (e.g. Amphistegina, Bryozoans, Lithothamnion, *etc*).
- Sandy marl, which generally lies below the Leitha limestone, has a relatively smaller distribution. In places, there is a lateral link to the limestone. However, it is of the great stratigraphic importance because a preliminarily study of a foraminiferal association indicated older levels of the Badenian Stage (the Lower Badenian Lagenidae Zone).
- Future biostratigraphic analyses of foraminifers and calcareous nannoplankton will clearly indicate the presence of Lower Badenian biozones (Lower or Upper Lagenidae Zone) and closely define the time of the marine transgression in this area. Besides, the precise biostratigraphic position of the Badenian limestone should be given.

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Резиме

Средње миоценска баденска трансгресија: нови докази са простора Врдничког угљеног басена (Фрушка гора, северна Србија)

Средње миоценска баденска трансгресија је један од најважнијих догађаја у миоцену који је оставио видљиве трагове на простору некадашњег Паратетиса. С тим у вези, много је доказа који указују на изненадне промене у режиму седиментације и по јужном ободу Панонског басена (BAKRAČ *et al*. 2010; KRSTIĆ *et al*. 2012; PEZELJ *et al*. 2013). Почетком средњег миоцена, као последица екстензионих фаза, створени су бројни грабени и ровови који су били испуњени морским синрифтним наслагама. Догађај је био условно синхрон на једној великој територији. Међутим, логично је веровати да је трансгресија захватила поједине делове Паратетиса у различито време (у распону од стотину хиљада година). У Србији, готово по правилу, кластични морски седименти бадена, дискордантно и трансгресивно леже преко старије подлоге, а врло често преко једне хетерогене, шарене серије старијег миоцена (има и другачијих мишљења – види KRSTIĆ *et al.* 2012). Слична ситуација је и раније констатована на простору Фрушке горе (ČIČULIĆ 1958; DOLIĆ 1961, 1998; ČIČULIĆ-TRIFUNOVIĆ & RAKIĆ 1976; PETKOVIĆ *et al.* 1976; RUNDIĆ *et al.* 2013). За разлику од северне стране планине, где је много лакше истражити те односе на самој површини, у околини Врдника су такви примери врло оскудни. Због тога су и урађена додатна теренска осматрања која су, уз подршку плитких бушотина у југозападном делу Врдничког угљеног басена, пружила нове доказе о присуству морске трансгресије на овом простору. Посебно је важно то што је по први пут документовано значајно подповршинско распрострањење морских седимената за које се раније није ни знало. На основу тога, дошло се до нових сазнања о геологији овог младог басена, тектонског рова формираног током миоцена и даље обликованог за време старијег плиоцена. Најважнији резултати су:

- На основу података добијених теренским истраживањима и анализом 14 плитких бушотина, извршена је реконструкција подповршинских односа на потезу Стрмоглавице–Велика Пећина, јужно од бање Врдник.
- У суперпозиционом поретку, присутне су следеће стратиграфске јединице: континентално-језерски доњи миоцен, морски средњи миоцен баден, горњи миоцен ?понт, те различите плеистоценске наслаге (првенствено тзв. сремска серија и лесно-палеоземљишне секвенце). Међутим, сматра се да велики део баденских наслага још увек није откривен. Нашим истраживањима је констатовано присуство више тектонских блокова који су резултат горње миоценске радијалне тектонике. Тим покретима је баденска карбонатна платформа издељена на блокове који су, у млађим фазама током плиоцена, додатно кретани и дислоцирани. Тако на неким издигнутим блоковима (бушотина Б-7), директно преко бадена належу квартарни седименти, што указује да знатан степен ерозије. Супротно томе, постоје и релативно спуштени

блокови где су осим бадена утврђене и друге неогене јединице (бушотина Б-4).

- У стратиграфском смислу, постоји трансгресиван и дискордантан однос морских наслага бадена преко старијих јединица (на нашим примерима само преко континентално-језерске Врдничке серије). Такав однос упућује на присуство напред наведене морске трансгресије и на овом простору.
- Анализом бушотина, утврђено је да постоји значајно подповршинско присуство морских наслага бадена у различитим фацијама, али је доминантно плитко, карбонатно развиће које указује на присутво једне релативно уске и издужене карбонатне платформе правца пружања исток–запад (процењена дужина од преко 1200 m а ширина до 250 m). У појединим бушотинама, дебљина карбоната достиже 70 m (Б-11).
- На основу прелиминарне палеонтолошке анализе (црвене алге, бриозое, мекушци, фораминифере и др.), може се рећи да је карбонатна платформа (рампа) више присутна у млађем бадену, него за време старијег и средњег бадена. Депоновање оваквих наслага (до 98 % $CaCO_3$) везано је за тзв. средње миоценски климатски оптимум који је омогућио стварање сличних седимената на широком простору Паратетиса али и Медитерана (Böhme, M. 2003; Harzhauser & Piller 2007; Rögl *et al.* 2008).
- Међу овим наслагама, доминантни су тзв. лајтовачки кречњаци који, у зависности од доминантне фосилне компоненте, могу би подељени на неколико биофација (алгални, бриозојски, амфистегински, и др.). У палеоеколошком смислу, сви они указују на плитку, спрудну и субспрудну морску средину са релативно топлом, чистом водом и дубином од 5 до 40 m (Zuschin & Hohenegger 1998; Wiedl *et al.* 2012, 2013).
- Мање партије песковитих лапораца и неких кластита које су откривене у бушотинама Б-11, Б-15, Б-19 и Б-21 а испод лајтовачких кречњака, имају мало опсервирано распрострањење. Међутим, извесно је да оне имају ванредно важну стратиграфску позицију. Наиме, прелиминарне одредбе присутне микрофауне фораминифера (*Orbulina suturalis*, *Globigerinoides trilobus, Lagena* и др. тј. асоцијација која одговара доњобаденској лагенидној зони) указују да се ради о најстаријим нивоима бадена и управо ти седименти леже трансгресивно преко шарених кластита Врдничке серије. О прецизнијој биостратиграфској детерминацији ових слојева није могуће говорити у овом тренутку (? доња или горња лагенидна зона) без детаљније квалитативне и квантитативне анализе поменутих фораминифера и кречњачког нанопланктона. На тај начин ће бити могуће и утврдити право време када се трансгресија и десила (оквирно пре 15 милиона година), слично ономе како је учињено и у неким другим подручјима по јужном ободу Панонског басена (Ćorić *et al.* 2009; Hohenegger *et al.* 2009; Pezelj *et al.* 2013).

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Pseudoclypeina? *crnogorica* Radoičić, 1972 – Stratigraphic revision and taxonomic note on a little known dasycladalean alga from Montenegro

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Abstract. *Pseudoclypeina*? *crnogorica* was first described in 1972 from the Lower, Cretaceous limestone of the Njegoš Mt. area, Montenegro, Dinaric Carbonate Platform. It differs from other species of the genus *Pseudoclypeina* by its calcification pattern, the shape and relative length of the first and second order laterals, and by the presence in the type-material (a thin section containing the holotype) of sections standing for the sterile portion of the thallus. This is why in this paper, the generic name is left in open nomenclature. On this occasion the species, whose presence is also reported from southern Iran, is re-described and better illustrated, based on material originating from other outcrops in Montenegro. The stratigraphic position is reviewed as well. *Pseudoclypeina*? *crnogorica* occurs in shallow water inner platform facies of early Neocomian age, along with *Selliporella neocomiensis*.

Key words: Dasycladalean (green algae), *Pseudoclypeina*? *crnogorica*, Neocomian, Dinaric Carbonate Platform, Montenegro.

Апстракт. Дазикладалеан *Pseudoclypeina*? *crnogorica,* описана 1972., потиче из доњокредних седимената Његош планине у Црној Гори (Динарска карбонатна платформа). *P.*? *crnogorica* разликује се од других врста рода *Pseudoclypeina* по типу калцификације, облику и димензијама примарних огранака као и присуством дијелова који одговарају млађем стерилном дијелу талуса. Стога је ова врста приказана у отвореној номенклатури генеричког имена. Дат је потпунији опис типског и другог материјала уз бројне илустрације. *P.*? *crnogorica* јавља се у плитководним фацијама неокома платформне унутрашњости, у слојевима у којима се јавља и *Selliporella neocomiensis.* Осим у Црној Гори, нађена је у седиментима исте старости у јужом Ирану.

Кључне ријечи: Dasycladalean (зелене алге), *Pseudoclypeina*? *crnogorica*, неоком, Динарска карбонатна платформа, Црна Гора.

Introduction

Lower Cretaceous, shallow water sediments of the shouthern Montenergro (NW–SE belt), Dinaric Carbonate Platform, contain an abundant flora of dasycladalean algae and subordinated foraminiferal fauna, especially in an interval covering part of the Neocomian. No less than six species of dasycladalean algae were originally described from this area. The aim of this paper is to revise the age and, based on yet unpublished material, provide new insights on the taxonomy of one of these species, the little known *Pseudoclypeina*? *crnogorica* Radoičić, 1972.

P.? *crnogorica* was originally described from undifferentiated Lower Cretaceous deposits, found in the Srijede area and forming the NE flank of the Njegoš Mt. anticline (Fig. 1). The core of the anticline consists of Jurassic and Cretaceous shallow water carbonates. The Jurassic succession, dated Lias to uppermost Malm (*Clypeina jurassica* Zone), includes a short stratigraphic gap laterally and partly corresponding to pre-Late Kimmeridgian bauxite deposits. The northeastern flank of the anticline is distorted by a longitudinal fault, along which late Malm and Neocomian Cretaceous sediments are in tectonic contact. The stratum typicum of *P.*? *crnogorica* is a limestone sampled at observation

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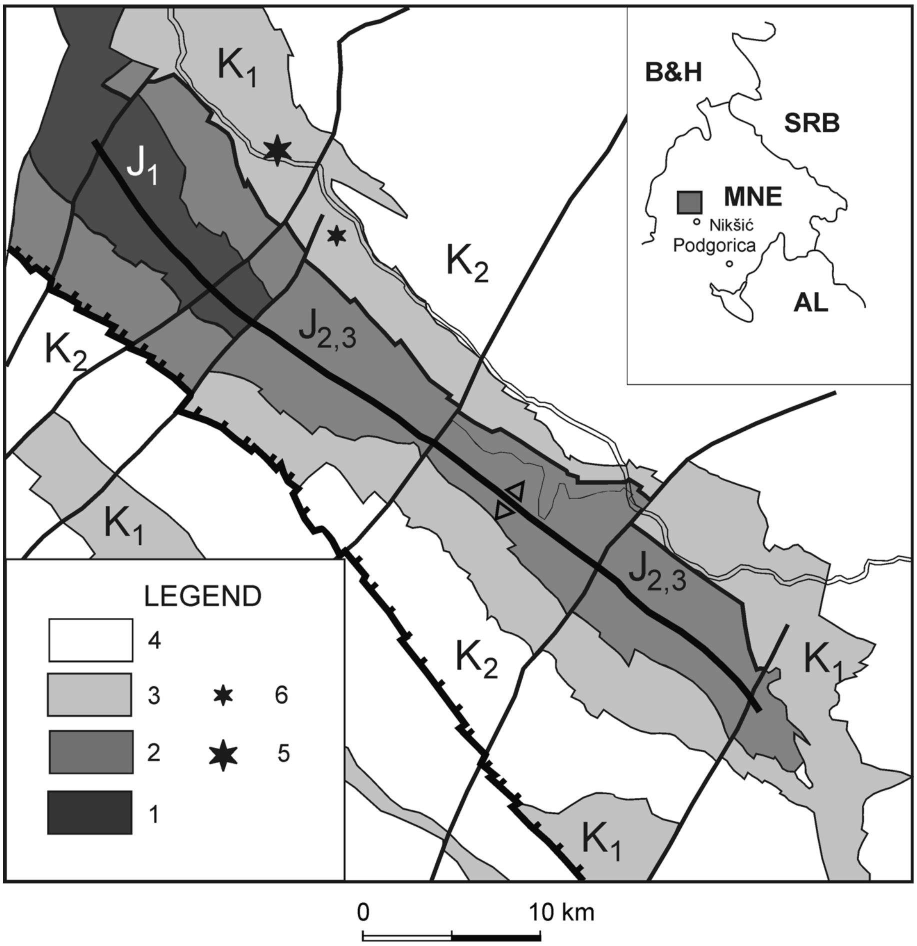

Fig. 1. Geological map of the Njegoš Mt. anticline, from the Geological Map Sheet Nišić , 1:100000 (Vujisić & Palinkašević, 1975), simplified. Legend: **1,** Lias; **2,** Middle and Upper Jurassic; **3,** Lower Cretaceous; **4,** Upper Cretaceous. Left star the type level.

point N° 1011b/1963 of the mapping team, on the Nikšić–Gacko road, NE flank of the anticline. Originally, it was erroneously assigned to the "Zone with *Salpingoporella melitae* and *Likanella danilovae* (Barremian–Lower Aptian)" [not "Barrémien-Aptien supérieur. Associée à *Salpingoporella melitae* et *Likanella* ? *danilovae"* (Bassoullet *et al.* 1978, p. 217)], because the two species were found in some other observation points. At that time, data enabling to date the NE flank of the anticline from the Neocomian was missing.

In many areas of western Montenegro, the Jurassic–Lower Cretaceous stratigraphic column is more or less reduced due to frequent subaerial exposures of different duration, resulting in the presence of significant stratigraphic gaps corresponding or not to the presence of white bauxite (Radoičić & Vujisić 1970; Radoičić 1993). One of such successions, with white bauxite ranging from the Neocomian to the Upper Albian–Cenomanian, is found in the Velimlje area, south of the Njegoš Mt. The lower–middle part of the Neocomian column, with numerous subaerial exposures consists, first of a limestone containing *Daturelina costata* and *Campbelliella striata*, followed by a coprogenous limestone with *Salpingoporella annulata*, coprolites and rare foraminifers and, finally by a limestone with fragments of an unknown dasycladalean alga later identified as *Pseudoclypeina*? *crnogorica*.

In the region of Prekornica and Lebršnik Mts, in northern part of the Geological map sheet Titograd at scale 1:100000, the "Ttitonian–Valanginian" limestone-dolomite succession ("J/K") is largely distributed, transgressive on the Upper Triassic or Triassic-Liassic deposits (Živaljević *et al*. 1971, 1973). Location is in the southernmost part of the large Nikšićka Župa bauxite bearing region, north of the Zeta intra-platform furrow. A Neocomian limestone containing *P.*? *crnogorica* was found on the road east of the Lebršnik Mt. Southward along the same road, two outcrops of a limestone containing *Selliporella neocomiensis*, *Clypeina neretvae* and *P.*? *crnogorica* were sampled (the first sampling, near Lisac, is type locality of *S. neocomiensis*). In all known localities of Montenegro, *P.*? *crnogorica* occurs in Neocomian sediments, most probably dated Late Berriasian or Late Berriasian–Early Valanginian.

Genus *Pseudoclypeina* Radoičić, 1970.

Three species of the genus *Pseudoclypeina* have been described from southern Montenegro (Dinaric Carbonate Platform): *P. cirici* Radoičić 1975, non 1970, the genotype, *P. farinacciae* Radoičić 1975, non 1970, both from the Upper Kimmeridgian, and *P.*? *crnogorica* Radoičić 1972, from the "Barremian–Lower Aptian" (now dated Neocomian). Because *P. cirici* differs from the other two species in having three orders of branches, Bassoullet *et al.* (1978), suggested that it would "préférable de signaler dans la diagnose du genre que *Pseudoclypeina* peut présenter deux ou trois ordres de ramification." Which, at once, is accepted in the present paper.

A new species, *Pseudoclypeina distomensis*, was introduced by Barattolo & Carras (1990) from the Lower Kimmeridgian of the Parnassus Carbonate

Platform, Greece. Accoding Barattolo and Carras "The 'tertiary branch', which Radoičić's diagnosis of *Pseudoclypeina* is referred to, is not considered in such a manner for the following reasons: it originates without ramification (absence of ramification); it is on the same extension of the secondary branch; branches of a same order bearing narrowings are already known and have been accepted by former authors [e.g. *Palaeodasycladus mediterraneus* (PIA)]".

In the opinion of the present first author (RR), the tertiary branch (lateral, segment) of *Pseudoclypeina cirici* (in prolongation of secondary which has integral inner calcification including mould of reproductive organ and the pore at the top) is rarely together preserved due to brittle joint with secondary. This part of the skeleton has the form to which term branch (lateral, segment) is more corresponding, in the same way as the term "narrowing" (constriction) more corresponds to *Pseudoclypeina distomensis.* Such distinction may be irrelevant if the biological function is the same, i. e. protection of the fertile organ.

Both species, *P. cirici* followed by *P. distomensis* occur in the shallow-water, Late Jurassic succession of the Distomon area, Parnassus Carbonate Platform. In the nearby Kallidromo Mt. they occur together as well (recent unpublished data, N. Carras). In the future, a detailed study may show to what extent the two species are reciprocally related.

Pseudoclypeina*? *crnogorica RADOIČIĆ, 1972

Fig. 2; Pls. 1–3; Pl. 4, Figs. 1, 2, 6

1972 *Pseudoclypeina crnogorica* sp. nov. – RADOIČIĆ, p. 365, figs. 1a–c.

Diagnosis. Thallus cylindrical, relatively large, the main stem bearing regularly spaced shallow funnel-shaped whorls of numerous laterals. Primary laterals ovoid, bearing a tuft of 4–6, rather large and long secondary laterals, gradually widened outwards and no further ramified. Primary and second order laterals equally inclined upwards. Calcification articulated, individually coating the whorls of laterals. Reproductive organs (cysts) not observed, presumably located in the primary laterals (cladosporous type).

Notes on the generic attribution. *Pseudoclypeina*? *crnogorica* differs from other species of the genus in the type of calcification, comparatively standard (originally aragonitic), made of an external coat of colorless sparry calcite. By contrast, in *Pseudoclypeina cirici*, *P. farinacciae* and *P. distomensis* an inner, yellowish coat of calcite is present, strongly recalling if not identical to the calcification pattern found in *Clypeina jurassica*. The thallus of *P.*? *crnogorica* is comparatively rather small, with a smaller number of laterals per whorl, noting that in *P. farinacciae* other biometrical values are incomplete because the skeleton is altered by dissolution. Finally the size ratio between primary and secondary laterals is almost opposite, denoting a substantial difference. This is why in this paper we prefer to put the species in open nomenclature.

Quoting BUCUR (2013) "*P. crnogorica*, the fourth species of the genus *Pseudoclypeina*, differs from the other species not only in its calcification pattern, i.e., blocky sparite, but also in the size ratio between the primary and secondary laterals. The primary laterals are half the length of the secondary ones and ovoid in shape; this is not typical for the genus *Pseudoclypeina*, and makes the assignment doubtful. Based on the morphology and size ratio of the laterals, this species is more likely to be affiliated to *Selliporella*, as emended by BARATTOLO *et al.* 1988. The general morphology of the thallus broadly resembles that of *Selliporella neocomiensis* (see BUCUR & SĂSĂRAN, 2003)". In *P.*? *crnogorica* however, the secondary laterals are phloiophore (widening out), as compared to pirifere (the opposite) in *Selliporella*. A possible transfer to *Dissocladella* is all the same rejected, because of different morphology and primary to first – second order laterals length ratio. That is why we prefer, at the moment, to assign the species with doubt to the genus *Pseudoclypeina*, avoiding creating another genus based on insufficient data. For the moment this standpoint is shared (pers. comm.) by two algologists, namely Filippo Barattolo (Naples) and Ioan I. Bucur (Cluj).

Description and comparisons. Based on available material, *P. crnogorica* shows a moderate dimensional variability of the following characters. External diameter (D) 3.5–4.4 mm; inner diameter (d) 1–1.3 mm; spacing of whorls (h) 0.9–1.0 mm; dimension of primary laterals max. 0.40×0.30 mm (proximally compressed); length of secondaries (l') 0.75–0.80 mm, with a distal diameter (p') of 0.275 mm. Number of primaries per whorl (w) 20–22. Upward inclination (α) of the primary laterals approximately 40° to the horizontal plane.

Two singular sections are illustrated in Pl. 3: Fig. 4 shows the oblique section of a fragment of whorl with smaller primaries, sparse and long secondaries); Fig. 5 shows the tangential section of strongly tilted second order laterals in cup-like arrangement. Most probably, these two sections belong to the youngest, sterile portion of the thallus, in a way similar to some recent genera. In the studied material the calcified main stem is not preserved. Membranes of the primary and secondary laterals are seldom preserved as a thin micritic coat (Fig. 2, the holotype). Calcification, made of colorless sparry calcite enclosing the primary and secondary laterals, becomes thinner at the thallus periphery and is usually not preserved distally. Partial recrystallization occurs, stronger around the top of the primary and proximal portion of the secondary laterals. Seldom, all of a whorl or fragment of whorl is completely recrystallized (Pl. 2, Fig. 3; Pl. 4, Fig. 2).

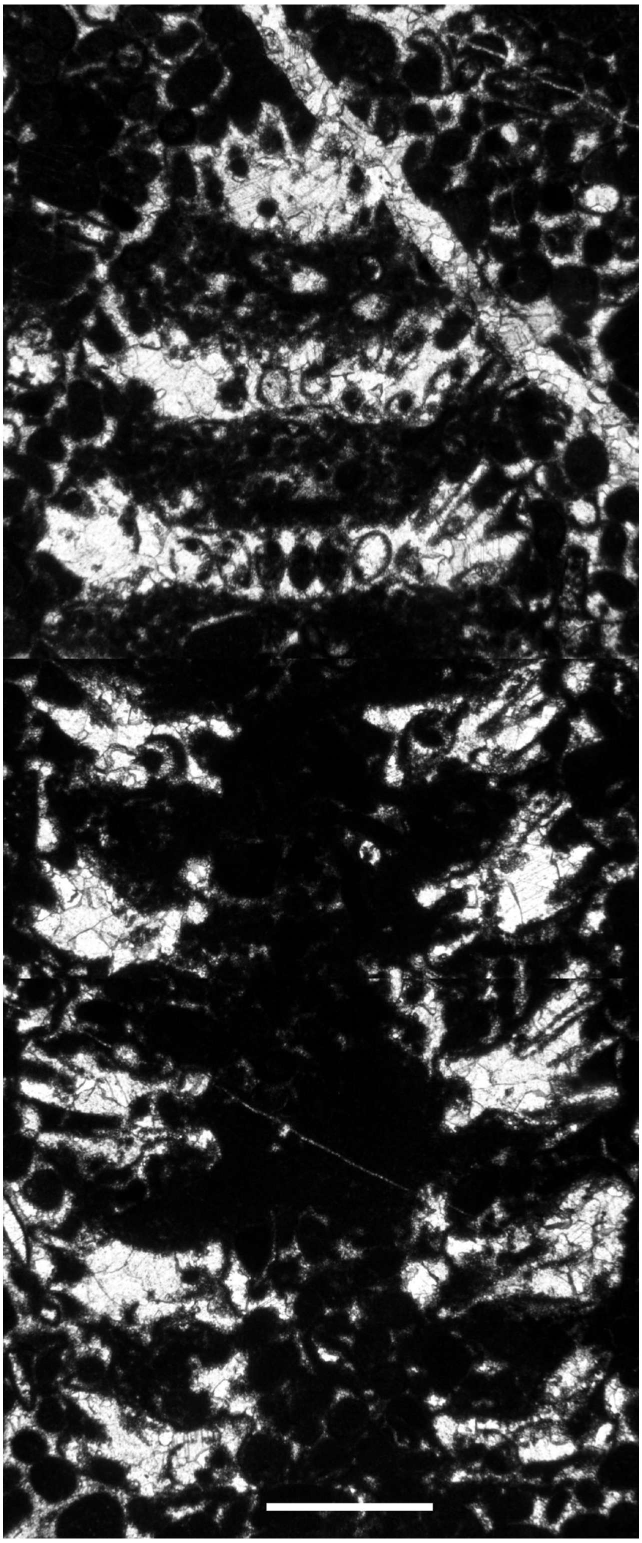

Fig. 2. *Pseudoclypeina*? *crnogorica* RADOIČIĆ, 1972, the holotype. Sub-axial section cutting eight whorls. The micritic membrane coating the first and second order laterals is especially well preserved. Thin section RR1927. Sterile parts of the thallus: see Pl. 3, figs. 4, 5.

Located in the Srijede area, the type-level of *P. crnogorica* consists of an inhomogeneous limestone (wackestone, packstone, peloidal limestone, grainstone containing micrite lithoclasts). The species mainly occurs as isolated whorls and fragments. From this bed, 11 thin sections were made from sample 07753a (RR1922-1925/1-1926/1-1930). Also six thin sections were made from sample 06230 (RR1794-1795/1-1798) originating from another, neighboring location. Finally, two thin sections were made from sample 03669 (RR1542,1543) originating from the Lebršnik Mt. area and one thin section from sample 03681a (RR1567) south of Lebršnik.

Algae labeled *Dasycladacea* sp. by FOURCADE *et al.* (1972, pl. 2, figs. 5–8) illustrates a specimen originating from the upper Barremian of Benizar–Otis area, southeast Spain, which has been included in *P. crnogorica* by BASSOULLET *et al.* (1978, p. 217). The same taxon, most probably, was illustrated by MASSE (1995, pl. 2, fig. 16) under the name of *Pseudoclypeina* sp., from the upper Barremian of Orgon, SE France. Compared to *P.*? *crnogorica* the calcification pattern of these specimens is the same but the shape of the primary laterals differs (elongated versus ovoid), and the length ratio of the first and second order laterals is the opposite, indicating a new taxon.

Stratigraphic and geographic distribution. In Montenegro, *Pseudoclypeina*? *crnogorica, Selliporella neocomiensis* and *Clypeina neretvae* occur in an inner platform limestone-early diagenetic dolomite interval presumably dated Upper Berriasian–Lower Valanginian. Besides the foregoing species, *P. crnogorica* is associated with common *Salpingoporella annulata*, *Salpingoporella* spp., *Clypeina* spp., some other small and undetermined species, fine algal debris, *Favreina* spp. and microgastropods. In southern Montenegro, locations form a discontinuous belt extending from northwest of Nikšić to the south-east, in the mountains area north of Podgorica (Titograd).

P.? *crnogorica* was presented by BERNIER *et al.* (1979, pl. 1, figs. 9–11) as *Pseudoclypeina* aff. *crnogorica* from Kimmeridgian–Portlandian of Mount Kanala, Gavrovo Massive, Greece, associated with foraminifer *Anchispirocyclina neumannae* n. sp. Than described the new foraminifer species *Anchispirocyclina neumannae* originates from "Portlandian supérieur (selon H. TINTANT, in M. RAMALHO 1971)" of Cap d'Espichel, south of Lisbon, Portugal.

Besides Montenegro and Greece, specimens looking alike *P*?. *crnogorica* are found in the Zagros fold and thrust belt of Southern Iran, in an interval dated Late Berriasian–Early Valanginian (HOSSEINI *et al.* 2013).

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Резиме

Pseudoclypeina? *crnogorica* Radoičić, 1972 - стратиграфска ревизија и биљешка о таксономији мало познате дасикладалеан алге из Црне Горе

Доњокредни плитководни седименти Динарске карбонатне платформе у јужној Црној Гори (појас СЗ–ЈИ), садрже бројну алгалну флору уз прилично сиромашну фораминиферску фауну, особито у једном интервалу неокома. Из доњокредних седимената овог подручја описано је шест нових дазикладалеанских врста. Предмет овог текста је стратиграфска ревизија и детаљнији приказ непубликованог материјала значајног за таксономију једне од ових врста - мало познате врсте *Pseudoclypeina? crnogorica.*

Pseudoclypeina? _crnogorica_ Radoičić, 1972
Pl. 1–3, pl. 4, figs. 1, 2, 6

1972 *Pseudoclypeina crnogorica* sp. nov. – Radoičić, стр. 365, сл.. 1а–с.

Дијагноза. Цилиндричан, релативно крупан талус, са главном осом која носи правилно распоређене плитко-љевкасте пршљенове бројних грана. Примарни огранци овоидног облика дају 4–6 релативно крупних и дугих секундарних огранака који се поступно благо проширују према спољашњој површини, не гранајући се даље. Примарни и секундарни огранци истог су нагиба према централној оси. Калцификација артикулатна – пршљенови су појединачно обавијени. Репродуктивни органи (цисте) непознати, вјероватно смјештени у примарним огранцима (кладоспорни тип).

Упоређење и опис. *Pseudoclypeina*? *crnogorica* разликује се од других врста рода *Pseudoclypeina* по типу калцификације коју чини спољашњи спари-калцитски омотач. Друге врсте, *P. cirici, P. farinacciae* и *P. distomensis* карактерише унутрашњи омотач жућкастог калцита који је веома сличан ако не и идентичан калцификацији врсте *Clypeina jurassica*. *P.*? *crnogorica* има талус мањих димензија, са мањим бројем огранака. Поменуте разлике су разлог што се у овом тексту *crnogorica* оставља у у отвореној родовској номенклатури, да би се, за сада, избјегло увођење новог рода на основу недовољно података.

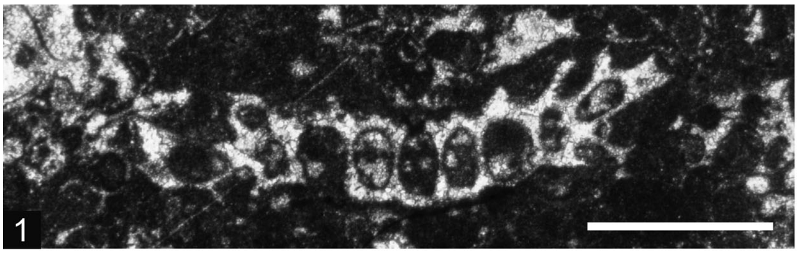
Два пресјека приказана на табли 3, сл. 4 и 5 приписују се најмлађем стерилном дијелу талуса. Мембрана примарних и секундарних огранака ријетко је сачувана као танак микритски омотач (сл. 2, холотип). Калцификација безбојног спаритског калцита обухвата примарне и секундарне огранке, на површини талуса најчешће није очувана. Прекристализација је обично јача у врху примарних и проксималном дијелу секундарних огранака, рјеђе су фрагменти пршљенова или читави дјелови талуса сасвим прекристалисали.

Географско и стратиграфско распрострањење. Приказани материјал потиче из четири локалитета у јужној Црној Гори. Типски локалитет и локалитет у његовој близини налазе се у подручју Сриједе на сјеверном крилу антиклинале Његош планине, сјеверозападно од Никшића (сл. 1). Друга два локалитета налазе се у планинској области сјеверно од Подгорице, западно и југозападно од Лебршника. У овим локалитетима, као и у неким другим у којима је препозната, *P.*? *crnogorica* јавља се у неокомским седиментима, највјероватније горњег беријаса или горњег беријаса-доњег валендиса.

Осим у Црној Гори, примјерци веома слични ако не и идентични врсти *P.*? *crnogorica* нађени су у седиментима горњег беријаса-доњег валендиса Загрос појаса у Јужном Ирану (HOSSEINI *et al.* 2013)

PLATE 1
Isotypes of *Pseudoclypeina*? *crnogorica* RADOIČIĆ, 1972

Fig. 1.	Tangential section of whorl with, in the proximal part, laterally slightly compressed primary laterals, elliptic in section. Note the calcified membrane of primary laterals (black micritic line). Thin section RR1926/1.
Figs. 2–5.	Oblique sections of whorls. In Figs. 2, 3 recrystallization is stronger around the top portion of the primaries and proximal portion of the secondaries. Calcification is thinner in Fig. 5. Thin sections RR1924, 1928, 1925/1, 1925/1.
Figs. 6, 12.	Tangential sections of the secondary laterals. Thin section RR1926.
Fig. 7.	Fragment of whorl showing the ovoid first order laterals and long gradually widening outward secondaries; the section plane follows the inclination of laterals.. Thin section RR1926.
Figs. 8–11.	Fragments, tangential-oblique sections cutting some of the primary and secondary laterals. Thin sections RR1928, 1951/1, 1927, 1929.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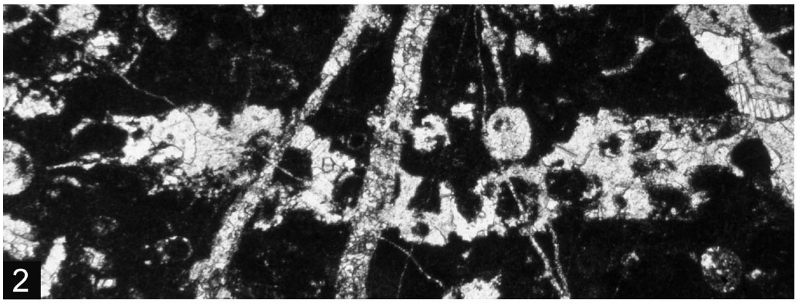
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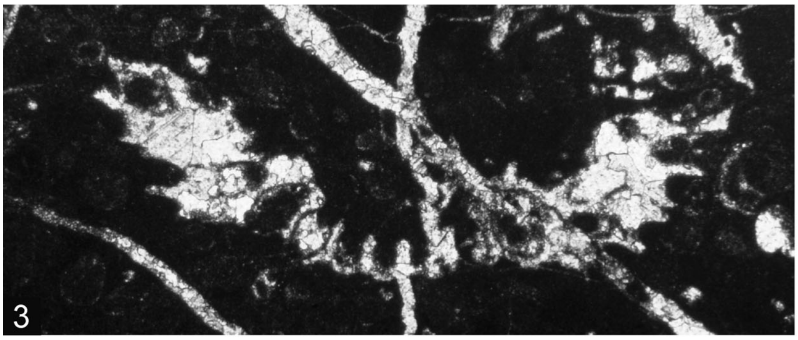
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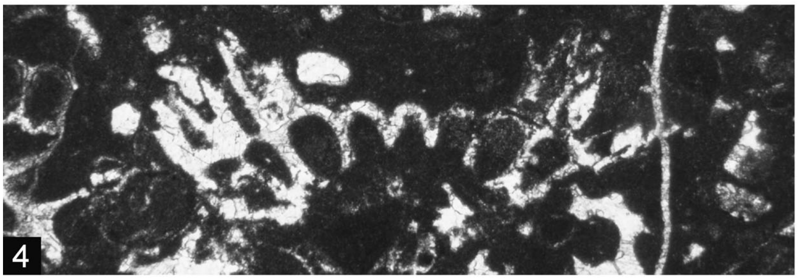
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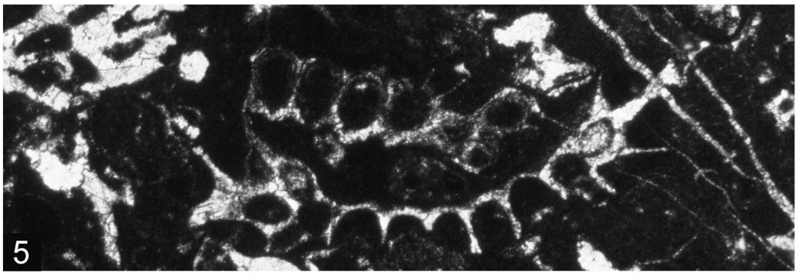
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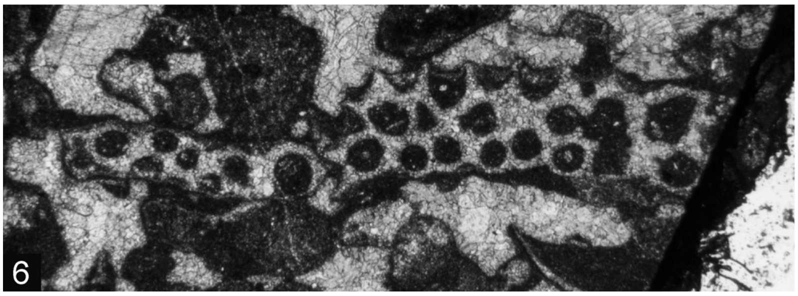
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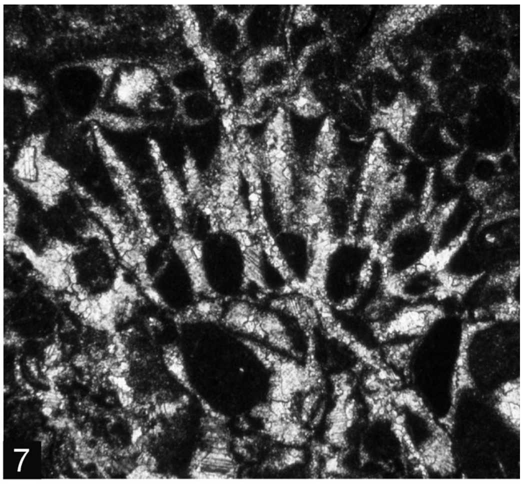
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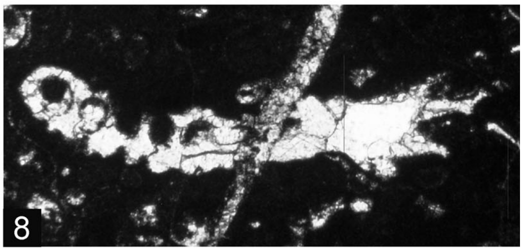
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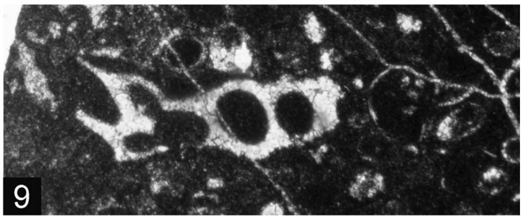
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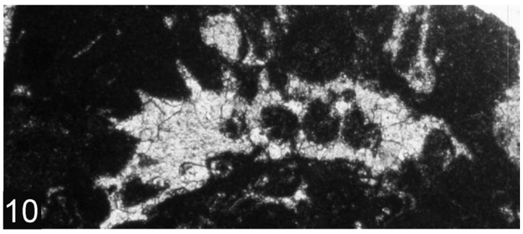
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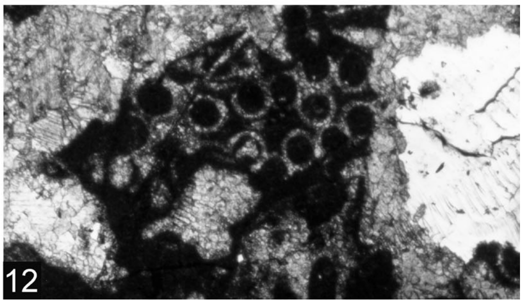
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Plate 2
Pseudoclypeina? *crnogorica* Radoičić, 1972

Fig. 1. Tangential section of a partially recrystallized whorl. Note the micritic membrane in transverse sections of two primary laterals, and the more recrystallized proximal portion of the secondaries. Thin section RR1926/1, isotype.

Fig. 2. Deep tangential section of a recrystallized whorl. Note the transverse sections of primary with micritic membrane. Thin section RR1796.

Fig. 3. Transverse section of a recrystallized fragment of a whorl. Thin section RR1796.

Fig. 4. Deep tangential-oblique section of a whorl. Thin section RR1796.

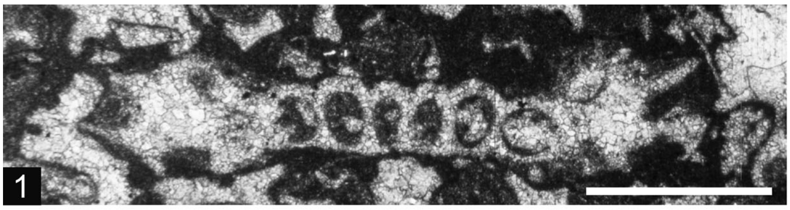
Figs. 5, 6. Subaxial sections, partly recrystallized. Note the upward inclination of the primary laterals. Thin section RR1795/1.

Fig. 7. Fragments of a whorl, fractured. Thin section RR1925, isotype.

Fig. 8–10. Fragments of whorls showing the primary laterals and the proximal parts of the secondaries. Thin sections RR1795/1, 1795, 1796.

Figs. 11, 12. Tangential sections of secondary laterals. Thin sections RR1725/1, 1926/1, isotype.

Fig. 13. Tangential-oblique section cutting the distal parts of three whorls in advanced degradation process. Note the micritic membrane in some of the second order laterals. Thin section RR1794.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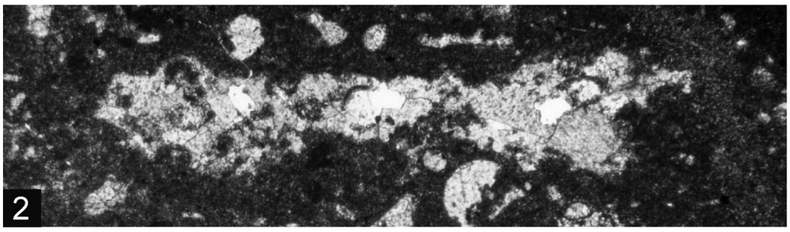
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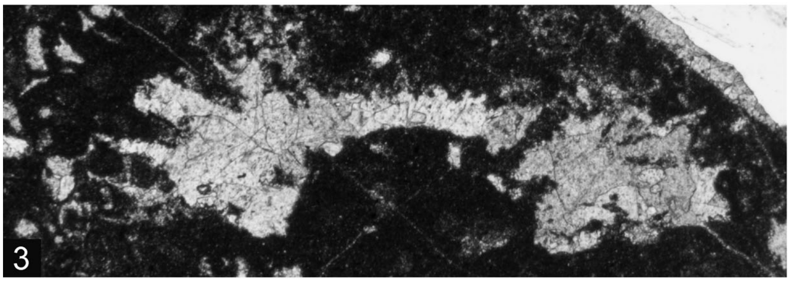
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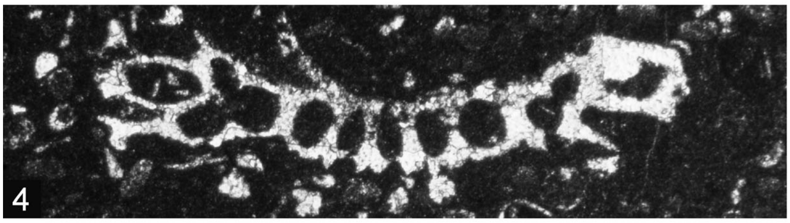
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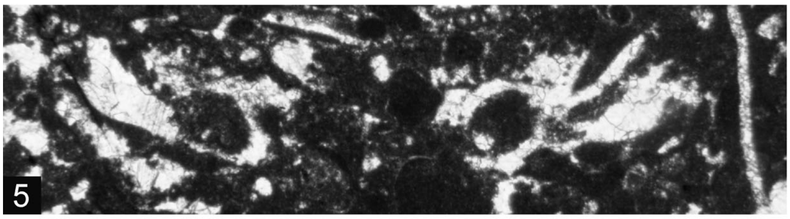
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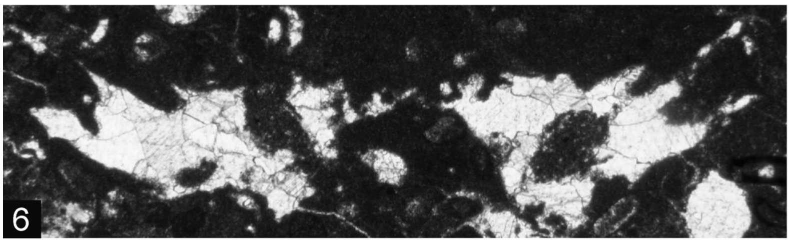
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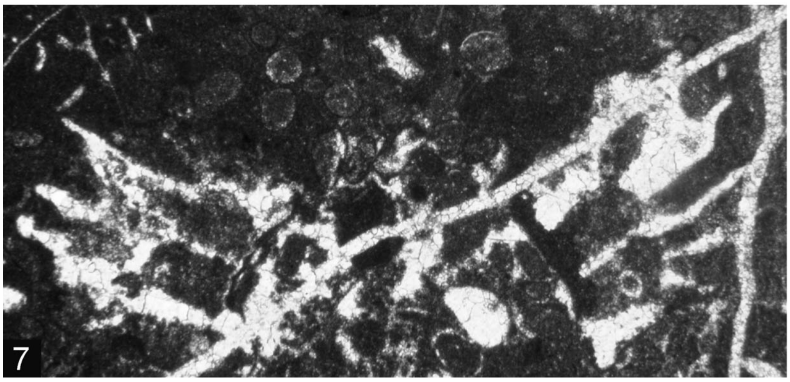
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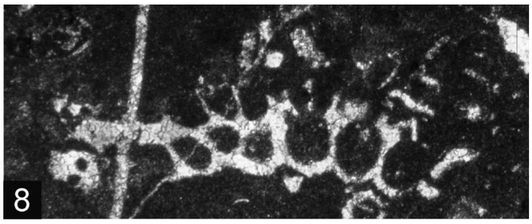
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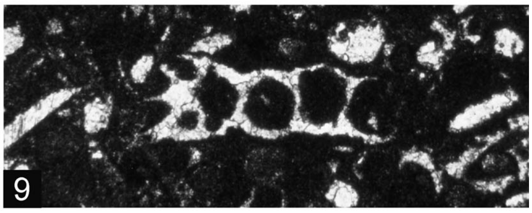
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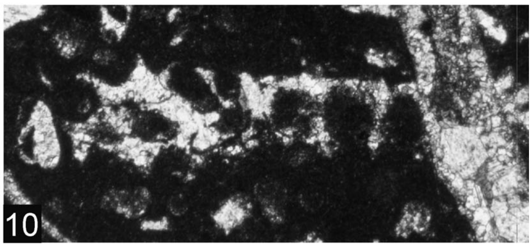
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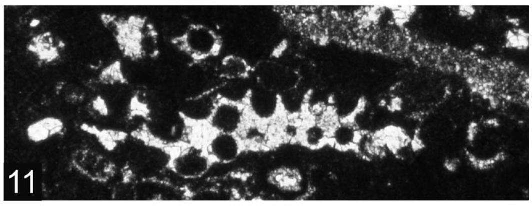
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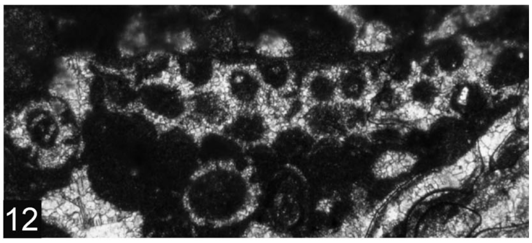
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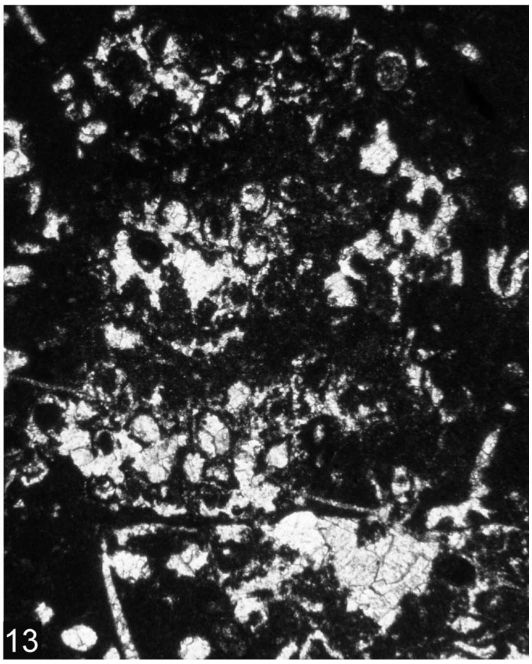
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Plate 3

Pseudoclypeina? *crnogorica* Radoičić, 1972

Fig. 1. Ill-preserved, fractured fragment of a whorl. The section plane more or less follows the inclination of the laterals. Left: most of the primary laterals are visible, as well as the slightly deformed secondaries and corresponding swollen distal part (arrow). Thin section RR1930, isotype.

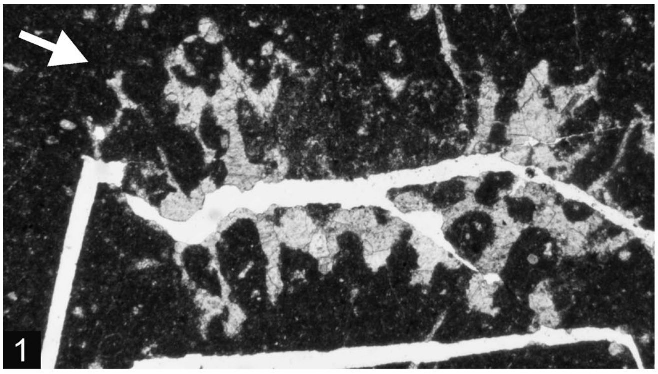
Fig. 2. Tangential-oblique section progressively cutting three, partly recrystallized whorls. Only the primary laterals are visible in the upper, deeper cutting, whorl. Thin section RR1794.

Fig. 3. Tangential section cutting three whorls showing different stages of preservation. Thin section RR1924, isotype.

Figs. 4, 5. Two sections interpreted as cutting the upper, sterile part of the thallus (4) with smaller primaries and (5) topmost, cup-like part of the thallus. Thin section RR1927 also containing the holotype.

Fig. 6. Fragment of whorl showing the primary laterals and poorly preserved proximal parts of the secondaries. Thin section RR1543.

Fig. 7. Tangential, slightly oblique section. Note the micritic membrane coating the primary laterals. Thin section RR1542.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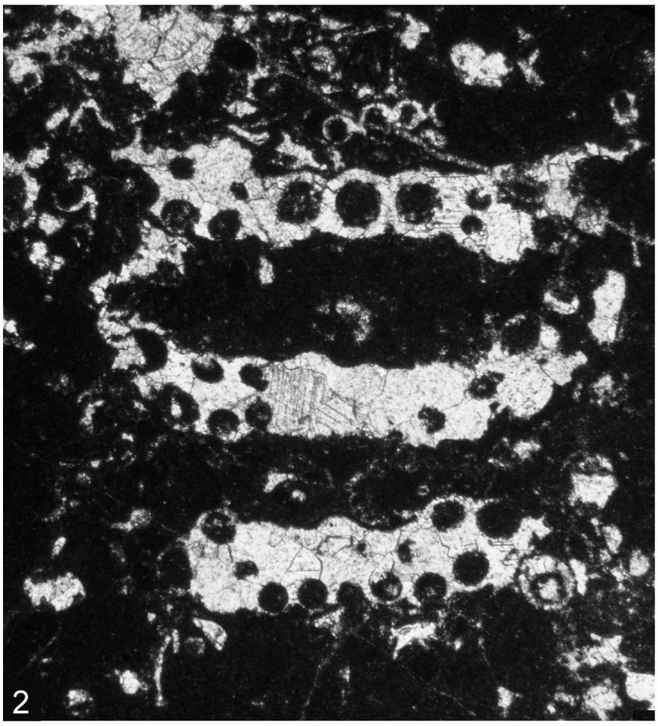
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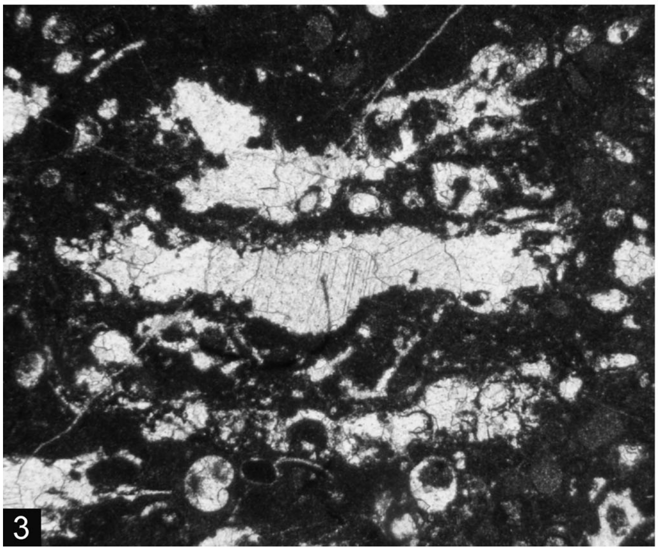
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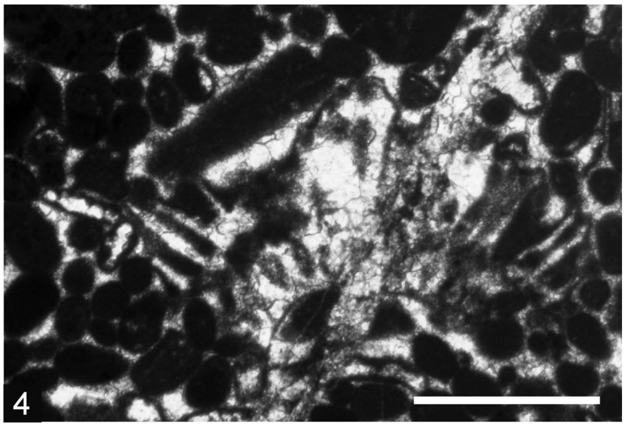
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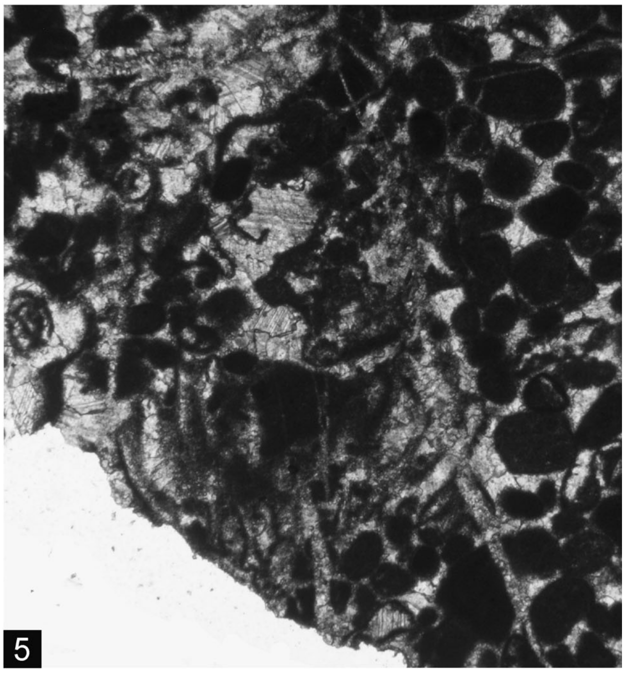
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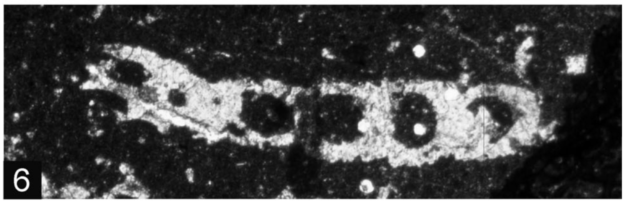
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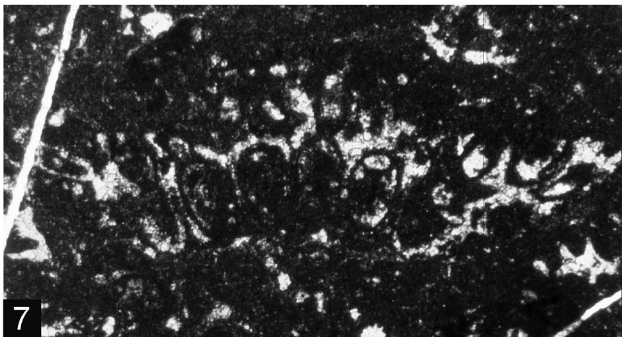
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PLATE 4

Fig. 1. Isotype of *Pseudoclypeina*? *crnogorica* RADOIČIĆ, 1972. Deformed, partly disintegrated and recrystallized part of a skeleton showing six whorls. Noteworthy, in this case some pores of the primary laterals are circular in section. Thin section RR1928.

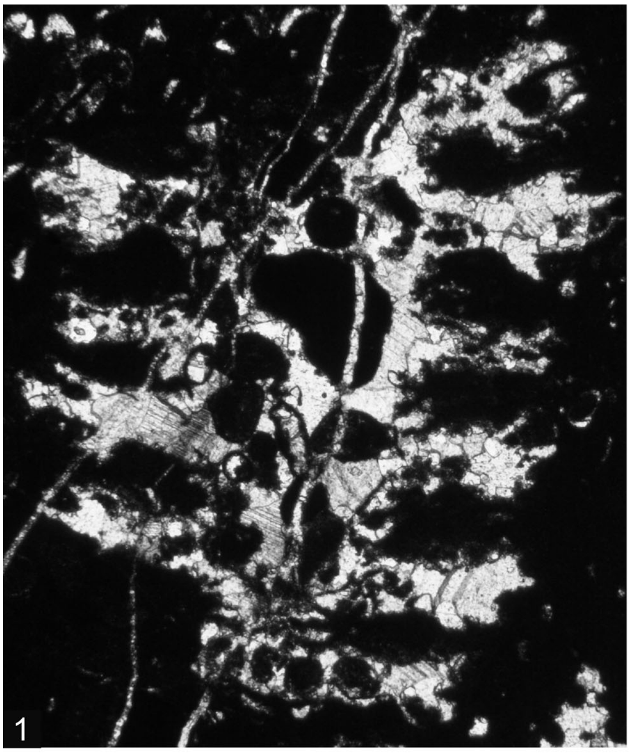
Fig. 2. *P.*? *crnogorica*. Fractured, deformed and completely recrystallized (large blocky calcite grains) of a specimen showing four whorls. Thin section RR1567.

Figs. 3, 4. Dasycladalean alga NK1 n. gen.?, n. spec. (informal designation). Arrows: dichotomous branching of the laterals. Thin sections RR1794, 1795/1, also containing *P.*? *crnogorica*.

Fig. 5. Presumably Dasycladalean alga NK1. The axial cavity covers part of the primary laterals, which are recrystallized and dichotomously branched at periphery. Thin section RR1924.(containing isotypes *P*? *crnogorica*).

Fig. 6. Isotype of *P.*? *crnogorica*. Transversal-oblique section of a partly recrystallized piece of thallus. Thin section RR1925/1.

Fig. 7. *Clypeina* sp. Thin section RR1795.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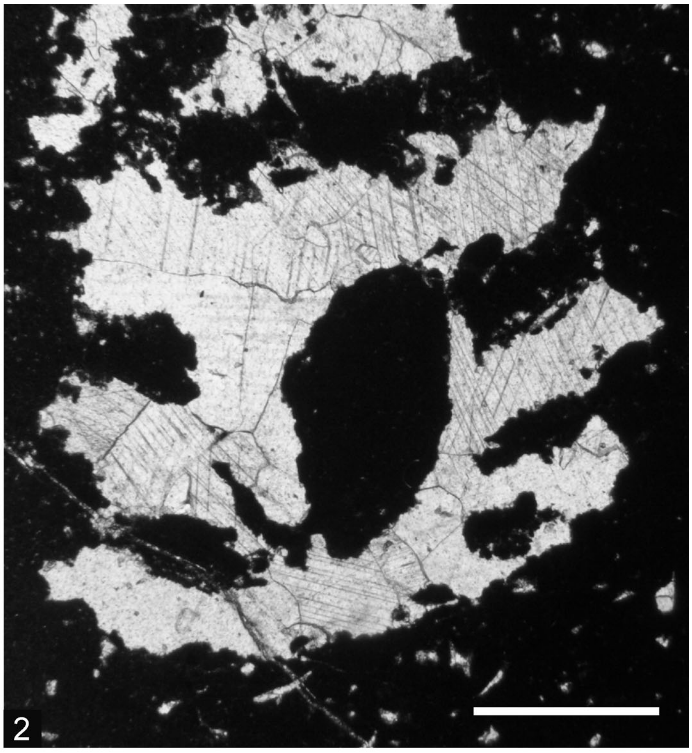
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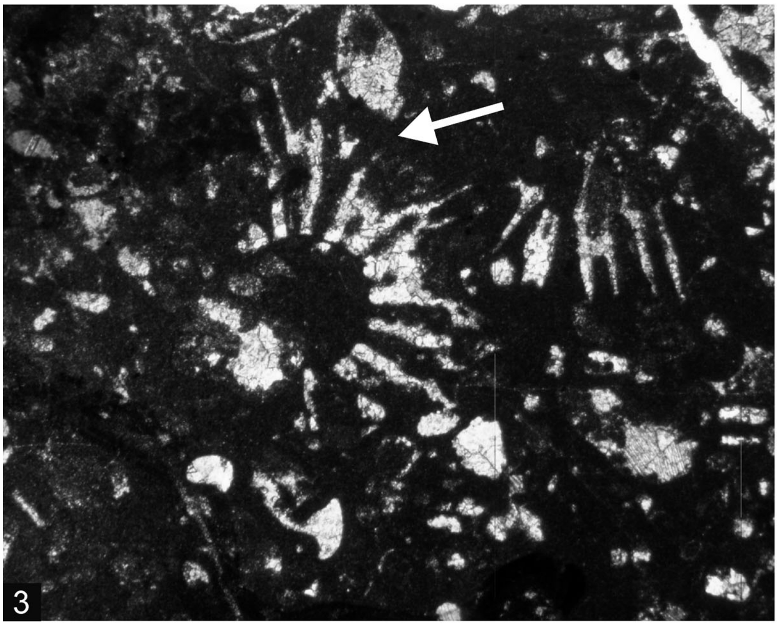
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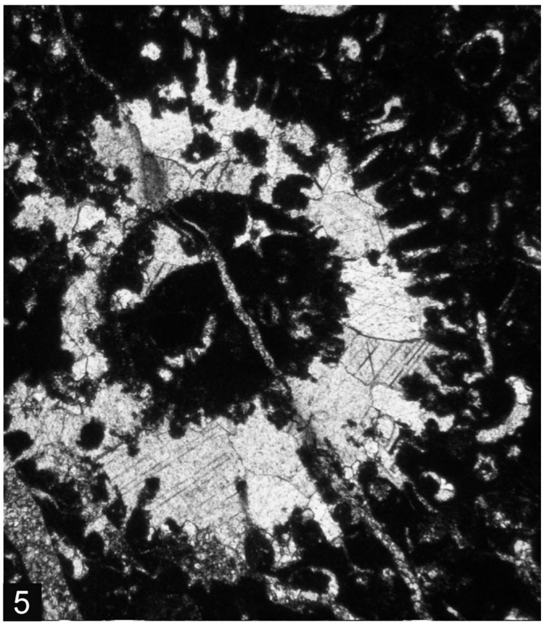
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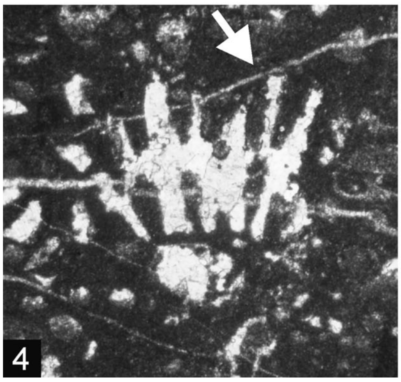
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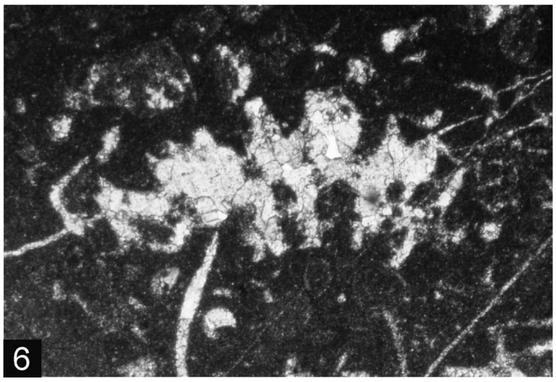
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Геолошки анали Балканскога полуострва Annales Géologiques de la Péninsule Balkanique	74	39–45	Београд, децембар 2013 Belgrade, December 2013

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Polymetallic Cu-Bi-(Pb-Zn-Co-Ag) mineralization of the Perin Potok locality near Bor, Serbia

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Abstract. Complex polymetallic Cu-Bi-(Pb-Zn-Co-Ag) mineralization of the Perin Potok locality occurs as disseminations and fine nests in quartz-ankerite-(sericite) veins. The veins are located in metamorphic rocks of the outer contact zone of the Variscan Gornjane Granitoid. The mineralization consists of (in decreasing abundance): chalcopyrite, aikinite, bismuth, galena, Ag,Bi-bearing tetrahedrite, sphalerite, cobaltite and an unnamed Bi_2Te mineral. All these phases form distinctive exsolutions and intergrowths and they simultaneously precipitated from a very complex hydrothermal fluid. Silver shows elevated contents in tetrahedrite (3.3–4.4 wt. % Ag), galena (0.9–1.1 wt. % Ag) and in the unnamed Bi_2Te mineral (0.9 wt. % Ag). Such high Ag concentrations can imply that Ag minerals could be also present. Minor amounts of rutile showing fine intergrowths with sericite also occur in this paragenesis. This is W-bearing rutile that shows zoning caused by up to 2.2 wt. % W. The studied mineralization is probably genetically related to the Variscan Gornjane Granitoid, although the possibility of derivation from the metamorphic basement should be also taken into account.

Key words: aikinite, bismuth, tetrahedrite, rutile, Variscan metallogeny, Gornjane Massive, east Serbia.

Апстракт. Комплексна полиметалична Cu-Bi-(Pb-Zn-Co-Ag) минерализација откривена на локалитету Перин поток образује импрегнације и гнездашца у кварц-анкерит-(серицитским) жицама које се налазе у контактној зони горњанског гранитоида с околним метаморфитима. Минерализацију чине (у опадајућој количини): халкопирит, ајкинит, самородни бизмут, галенит, Ag,Bi-тетраедрит, сфалерит, кобалтин и неименовани Bi_2Te минерал. Сви ови минерали образују изразита издвајања и прорастања и истовремено су депоновани из једног веома комплексног хидротермалног флуида. Сребро показује повећане концентрације у тетраедриту (3,3–4,4 мас. % Ag), галениту (0,9–1,1 мас. % Ag) и неименованом Bi_2Te минералу (0,9 мас. % Ag). На основу ових повишених концентрација Ag може се претпоставити да на испитивном терену постоје и минерали сребра. Рутил, који је у мањој количини такође присутан у овој парагенези, показује фина прорастања са серицитом. Овај W-обогаћени рутил показује зонарност узроковану садржајем волфрама до 2,2 мас. %. Испитивана минерализација вероватно је генетски повезана с горњанским гранитоидом, мада би могућност њеног порекла из околних метаморфита такође требало узети у разматрање.

Кључне речи: ајкинит, самородни бизмут, тетраедрит, рутил, херцинска металогенија, горњански масив, источна Србија.

Introduction

The locality of Perin Potok, situated about 10 km north-eastward of the town of Bor, has long been known as one of the occurrences of W-Mo mineralization in north–east Serbia. The mineralization is mostly represented by scheelite and molybdenite and, apart of these minerals, the presence of sulphides – chalcopyrite, pyrite and rarely arsenopyrite - was also reported (Savić 1956; Janković 1990). This W-Mo mineralization is generally interpreted as genetically related to the Gornjane Granitoid. This granitoid belongs to a belt of NE Serbia granitoids that were formed by Variscan orogenic/post-orogenic events (Urošević 1908; Simić 1953; Mihajlović-Vlajić & Markov 1965; Divljan & Divljan 1972). Both Variscan gran-

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itoids and their metamorphic basement are found to host numerous ore-bearing quartz veins with W, Au and sporadically with Cu, Fe and Pb-Zn mineralizations (Simić 1953; Kalenić *et al*. 1973, 1976). In this context, the true origin of these mineralizations (either magmatic or metamorphism-related?) remained poorly constrained.

In this study we report new data on the polymetallic mineralization occurring in the Perin Potok locality, in particular on the assemblage dominated by Cu-Bi-(Pb-Zn-Co-Ag) metallogeny. To our best knowledge, this locality represents the very first occurrence of such type of mineralization in north-east Serbia. By presenting textural and mineral chemistry characteristics of the observed ore paragenesis we want to provide better understanding of the formation of W-Mo-dominated mineralization in north–east Serbia. We also have reasons to believe that this association of metals could be present in economically significant proportions in this area, and can shed new light on the whole metallogeny of the entire region.

Geological Setting

The studied polymetallic mineralization occurs in a very complex area of the East Serbian Carpatho-Balkanides that represents an assemblage of the Lower Paleozoic terranes intruded by the late Variscan granitoids (e.g. Karamata & Krstić, 1996; Karamata, 2006). The Perin Potok mineralization is found along the southern contact zone between the Variscan Gornjane Granitoid and the surrounding metamorphic rocks of the Stara Planina–Poreč terrane. Further to the west there are occurrences of the Upper Cretaceous andesitic volcanics and volcaniclastics of the Timok Magmatic Complex that is famous of large porphyry-copper and epithermal-gold systems (e.g. Banješević, 2006; Kolb *et al*. 2013). A simplified geological sketch of the area is shown in Fig. 1.

Gornjane is a NNW–SSE elongated lens-shaped granitoid pluton that consists of quartz monzonite, granodiorite, quartz diorite, diorite and syenite displaying gradual transitions in composition (Divljan & Mićić 1960; Kalenić *et al*. 1976; Vasković *et al*. 2012). Central parts of the magmatic body are composed of quartz monzonite surrounded by granodiorite, while in the peripheral parts and contact zones dioritic rocks generally occur. This granitoid pluton contains numerous quartz veins, veins of pegmatite and aplite, and younger shallow granite intrusions. Vasković *et al*. (2012) reported the U-Pb zircon ages of 323.3 ±2.6 Ma to 305.8 ±3.6 Ma. These ages confirm that the emplacement of this granitoid massive occurred during the late Variscan events.

The metamorphic basement consists of the Rifeo-Cambrian to the Lower Palaeozoic units (Kalenić *et al*. 1976) composed of various metabasic and metasedimentary rocks. The locality of Perin Potok is located along the contact zone between the Gornjane Granitoid and the Lower Palaeozoic unit. The latter unit starts with conglomerates and continues with sandstones, siltstones, metamorphosed clays and phyllites.

The mineralization is found in up to 30 cm thick quartz-ankerite and subordinate sericite veins. The

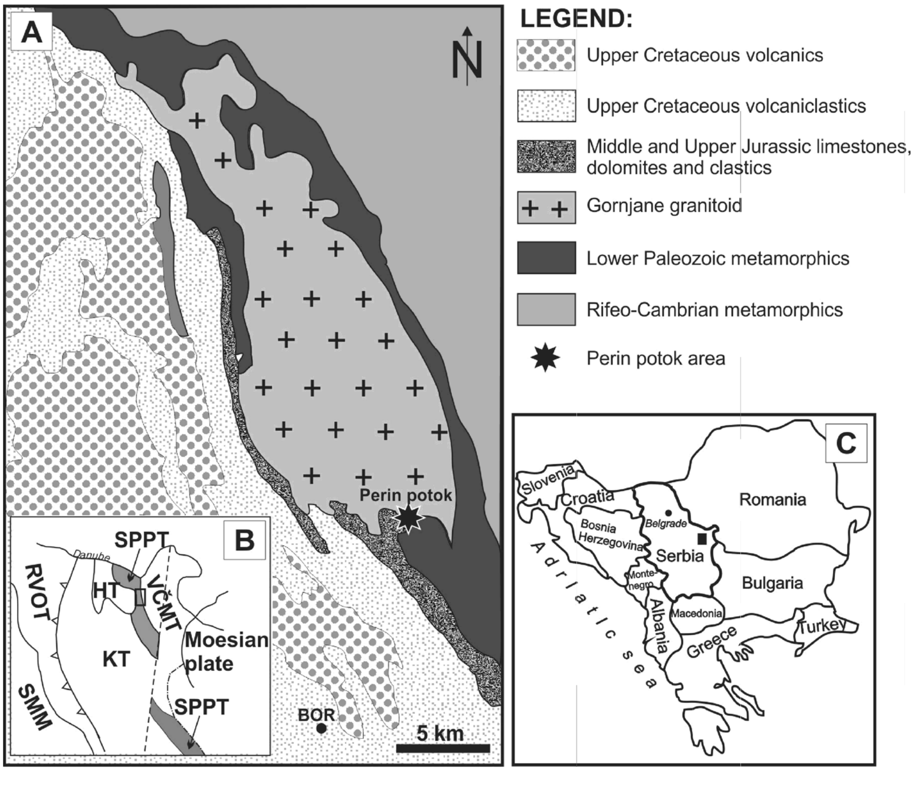

Fig. 1. **A,** Simplified geological map (Kalenić *et al*., 1976), **B,** Geotectonic division (Karamata & Krstić, 1996) and **C,** Geographical position of the studied area. Explanations: **SPPT,** Stara planina–Poreč terrane; **VČMT,** Vrška čuka–Miroč terrane; **HT,** Homolje terrane, **KT,** Kučaj terrane; **RVOT,** Ranovac–Vlasina–Osogovo terrane; **SMM,** Serbo-Macedonian massif.

veins can be found only in stream beds as stream flanks are covered by humus. They are mainly enclosed in adjacent metamorphic rocks. Sulphide minerals form disseminated mineralization and nests up to 5 mm in size in these veins.

Materials and Methods

Representative samples of the mineralized veins were routinely studied macroscopically and by reflected-light microscopy. Electron microprobe analyses (EMPA) of the ore minerals were obtained at the University of Belgrade – Faculty of Mining and Geology, using a JEOL JSM–6610LV scanning electron microscope (SEM) connected with INCA energy-dispersion X-ray analysis (EDX) unit. An acceleration voltage of 20 kV was applied. The following standards and analytical lines were used: pure copper (Cu*K*α), pyrite (Fe*K*α, S*K*α), ZnS (Zn*K*α), InAs (As*L*α), Ag_2Te (Ag*L*α, Te*L*α), InSb (Sb*L*α), PbS (Pb*M*α), pure bismuth (Bi*M*α), pure cobalt (Co*K*α), pure nickel (Ni*K*α), CdS (Cd*L*α), TiO (Ti*K*α) and pure tungsten (W*L*α). Detection limits of the applied EDX measurements were 2σ ~ 0.2 wt. %. Gangue minerals were determined by semi-quantitative analysis using internal standards.

Results

This complex mineralization is characterized by fine intergrowths of many sulphides (Fig. 2), among which chalcopyrite and aikinite predominate, whereas bismuth, galena, sphalerite, tetrahedrite and locally cobaltite are less abundant. In addition, fine exsolutions of an unnamed Bi_2Te mineral also occur in this assemblage, but only as rare grains up to 10 μm in size. Chalcopyrite and aikinite occur as irregular grains mainly up to 1–2 mm in size. Exceptionally,

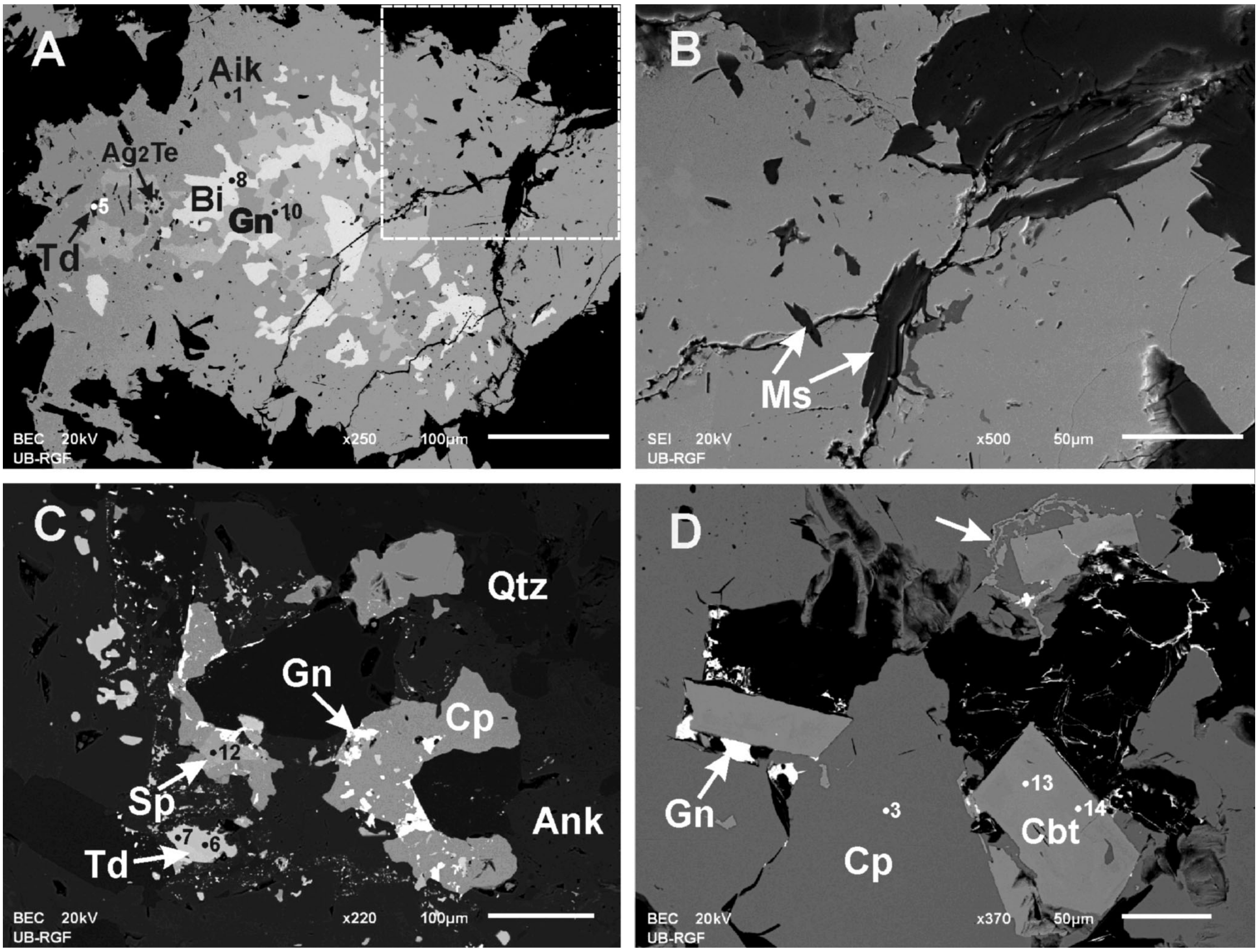

Fig. 2. Studied mineral assemblages from the Perin Potok locality (**A, C, D,** backscattered electron images; **B,** secondary electron images of detail marked by rectangle in A). Fine intergrowths of cobaltite with chalcopyrite in **D** are marked by the arrow. Dots and numbers represent single electron microprobe analyses given in Table 1. Symbols: **Aik,** aikinite; **Ank,** ankerite; **Bi,** bismuth; **Cbt,** cobaltite; **Cp,** chalcopyrite; **Gn,** galena; **Ms,** muscovite; **Qtz,** quartz; **Sp,** sphalerite; **Td,** tetrahedrite.

chalcopyrite can be up to 4–5 mm in size. Bismuth forms characteristic exsolutions in the central parts of aikinite grains (Fig. 2a). Tetrahedrite also forms exsolutions in aikinite (Fig. 2a), but it mainly appears as intergrowths with chalcopyrite, sphalerite and galena (Fig. 2c). Cobaltite forms individual subhedral to euhedral grains up to 0.1 mm in size or shows intergrowths with chalcopyrite (Fig. 2d).

Table 1. Results of electron microprobe analysis (wt.%) of the ore minerals from the Perin Potok locality.

Spot	Mineral	S	Fe	Cu	Zn	As	Ag	Sb	Pb	Bi	Co	Ni	Cd	Te	Total
1	Aikinite	15.3		11.0					39.0	35.3					100.6
2		15.0		11.2					39.1	35.1					100.4
3	Chalcopyrite	35.1		34.0											99.0
4		35.4	29.9	34.1											99.6
5	Tetrahedrite	23.9	30.1	32.1	4.1	0.4	4.4	26.3		6.1					99.3
6		25.0	2.0	35.2	5.1	6.5	3.3	19.8		3.3					99.9
7		24.3	1.8	34.0	5.8	4.1	4.0	22.3		3.5					99.4
8	Bizmuth		1.4							100.2					100.2
9	Unnamed Bi$_2$Te						0.9			76.2				22.0	99.1
10	Galena	12.7					0.9		85.6						99.2
11		12.8					1.1		85.3						99.3
12	Sphalerite	33.1	1.6		57.2								7.5		99.4
13	Cobaltite	21.0	3.8			43.6					31.2	1.0			100.6
14		22.4	6.8			41.7					28.1	1.3			100.3

Chemical compositions of all the above-mentioned ore minerals are given in Table 1. Aikinite, chalcopyrite and bismuth do not contain EMPA-detectable trace elements. Tetrahedrite displays chemical zoning caused by Sb-As solid solution. Apart of the essential elements, this mineral contains considerable amounts of silver (3.3–4.4 wt.% Ag) and bismuth (3.3–6.1 wt.% Bi). The presence of these metals characterizes this mineral as a variety of Ag,Bi-bearing tetrahedrite. The unnamed Bi$_2$Te mineral contains 0.9 wt.% Ag and shows Bi:Te ratio close to 2:1. There is no known mineral of such composition. However, as this mineral occurs in very small grains, its detailed determination was not possible. Galena contains 0.9–1.1 wt.% Ag. Sphalerite contains common amount of iron (1.6 wt.% Fe) and relatively higher amounts of cadmium (7.5 wt.% Cd). Cobaltite shows slight zoning caused by its common impurities of iron (3.8–6.8 wt.% Fe) and nickel (1.0–1.3 wt.% Ni).

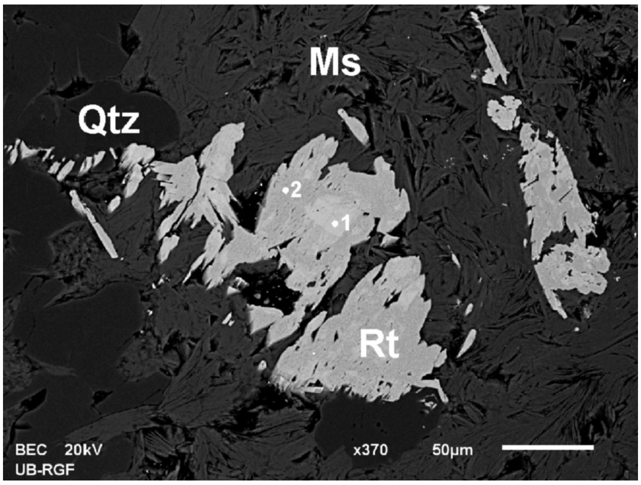

Fig. 3. Occurrence of W-bearing rutile at the Perin Potok locality (backscattered electron image). Dots and numbers represent single electron microprobe analyses given in Table 2. Symbols: **Ms,** muscovite; **Qtz,** quartz; **Rt,** rutile.

Negligible amounts of pyrite and pyrrhotite are also present. Pyrite occurs in anhedral to subhedral individual grains and in aggregates up to 0.3 mm in size, while pyrrhotite forms rare subhedral to euhedral grains up to 50 µm in size.

Minor amounts of rutile occur as irregular grains and aggregates up to 0.2 mm in size. Rutile shows fine intergrowths with sericite and displays crystal zoning caused by uncommonly high tungsten contents of up to 2.2 wt.% W (Fig. 3 and Table 2).

Table 2. Results of electron microprobe analysis (in wt.%) of W-bearing rutile from the Perin Potok locality.

Spot	O	Ti	Fe	W	Total
1	39.3	56.5	1.3	2.2	99.3
2	40.0	59.3	0.3		99.6

Sericite, i.e. fine-grained muscovite that is coeval with rutile (Fig. 3), appears within cracks in sulphide-bearing mineral aggregates (Fig. 2b). Thus, it could be concluded that this mineral assemblage formed in the stage of mineralization where sulphide minerals are simultaneously deposited with quartz and ankerite, whereas sericite and rutile precipitated in a subsequent paragenetic sequence of the same stage.

Discussion and conclusions

The above reported data suggest that minerals carrying Cu and Bi - chalcopyrite and aikinite, are the most abundant ore phases in the studied sample suite, whereas bismuth, galena, sphalerite, cobaltite and tetrahedrite are subordinate. All these ore minerals of Cu, Bi, Pb, Zn and Co, which form distinctive exsolutions and intergrowths, simultaneously precipitated from a complex hydrothermal fluid. This fluid was enriched also in additional elements of interest, especially in Ag, and in lesser degree in Ni and Te. The presence of Ag minerals is not revealed in this assemblage, but this precious metal occurs is considerable amounts in other ore minerals, principally in tetrahedrite and galena. Nickel occurs in cobaltite, while tellurium forms fine exsolutions of an unnamed Bi_2Te mineral. Sphalerite contains elevated contents of cadmium. Additionally, minor amounts of W-bearing rutile are also found. Thus, it could be suggested that this paragenesis was formed under high- to middle-temperature hydrothermal conditions from a complex Cu-Bi-Fe-Pb-Zn-Ag-Co-Ni-Ti-W-As-Sb-S-Te-bearing fluid. The presence of such very complex ore paragenesis indicates that, in addition to already known occurrences of W-Mo mineralization (SAVIĆ 1956), this area probably contains other types of mineralization. These types can be variable at relatively short distances and they may host so far undiscovered ore phases, especially Ag-bearing minerals. This is inferred from elevated contents of this metal, which are found in some minerals investigated by this study.

The metal budget of the studied mineralization probably derived from the Gornjane granitoid. However, as this mineralization was revealed in adjacent metamorphic rocks, it lacks clear spatial and genetic relationships of the mineralization with the granitoid. Thus, the origin of the mineralization from the metamorphic basement could be also considered. It is much less plausible that this mineralization is related to the Upper Cretaceous Timok Magmatic Complex because, this very well-studied Cu-dominated mineralization is not characterized by the presence of Bi minerals or by the ore mineral assemblage present here.

As already stated above, Cu, W, Mo and in lesser degree Pb mineralization is widespread in quartz- and pegmatite veins of the Gornjane Granitoid. Moreover, SIMIĆ *et al.* (1953) found the presence of cassiterite in some placers of the streams surrounding the Gornjane granitoid. They reported an association of W, Mo and Sn, and presumed that the presence of still undiscovered Bi minerals could complete the already known metal assemblage typical of granitoid rocks. The occurrence of Bi minerals reported by this study supports their speculation.

Partly similar mineralization regarding predominant metals was discovered in east Serbia only in the region of Stara Planina Mt. It is the Cu-Bi ore deposit of Aljin Do where vein ore bodies are found to occur in the large gabbro massive of Zaglavak, and this deposit is interpreted as having derived from the adjacent Variscan granitoids (JANKOVIĆ 1990).

On the other side, the Perin Potok mineralization occurs in quartz-ankerite-(sericite) veins located in metamorphic rocks that are generally rich in quartz and sericite. These metamorphic rocks are widespread in NE Serbia and represent also the basement of other granitoids in this region (SIMIĆ *et al.* 1953). Numerous ore-bearing quartz veins with W-, Au- and various polymetallic mineralizations are found in the metamorphic basement in other parts in NE Serbia (SIMIĆ 1953; KALENIĆ *et al.* 1973, 1976). For instance, there is a similarity of the ore vein type found in Perin Potok with those occurring near Neresnica because both contain ankerite (SIMIĆ 1953). All these occurrences were often explained as genetically related to Variscan granitoids, even though a clear spatial relationship between the mineralized veins and the granitoids lacks in many cases.

It is clear that the complex mineral association found in the contact zone of the Perin Potok locality needs further investigations. These studies must aim at better and more unequivocal constraining the genetic relations between the ore-bearing quartz veins and either the Variscan granitoids or the metamorphic basement. Moreover, the future investigations should examine the possibility that the associations of metals reported in this study may have economically significant occurrences in a wider area.

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Резиме

Полиметалична Cu-Bi-(Pb-Zn-Co-Ag) минерализација на локалитету Перин Поток у близини Бора, Србија

На локалитету Перин поток, који се налази у атару села Топла, око 10 km североисточно од Бора, а који је раније био познат по присуству W-Mo орудњења, откривена је комплексна полиметалична Cu-Bi-(Pb-Zn-Co-Ag) минерализација у кварц-анкерит-(серицитским) жицама. Ове жице дебљине до 30 cm налазе се у јужној контактној зони горњанског гранитоидног масива варисцијске старости и метаморфита који чине његову основу, при чему су жице откривене у метаморфитима који су у овом делу контактне зоне претежно изграђени од филита (сл. 1).

Ова комплексна минерализација карактерише се финим прорастањем сулфидних минерала (сл. 2), међу којима су најзаступљенији халкопирит и ајкинит, док се самородни бизмут, галенит, сфалерит, тетраедрит и кобалтин јављају у мањој количини. Поред наведених минерала, овај рудоносни полиминерални агрегат садржи и ретка зрна (до 10 μm) неименованог минерала Bi_2Te састава. Електронска микроанализа поменутих рудних минерала дата је у табели 1. Ајкинит, халкопирит и бизмутинит не садрже хемијске примесе. Тетраедрит показује зонарност узроковану Sb-As чврстим раствором, а овај минерал сложеног састава садржи у значајнијој количини и сребро (3,3–4,4 мас.% Ag) и бизмут (3,3–6,1 мас.% Bi), услед чега се може закључити да је реч о Ag,Bi-тетраедриту. Галенит такође садржи сребро у концентрацијама 0,9–1,1 мас.% Ag. Сфалерит садржи уобичајене примесе гвожђа (1,6 мас.% Fe) и релативно високе концентрације кадмијума (7,5 мас.% Cd). Кобалтин показује слабу зонарност узроковану примесама гвожђа (3,8–6,8 мас.% Fe) и никла (1,0–1,3 мас.% Ni). У испитиваној минерализацији присутне су и мање количине рутила, као и ретка зрна пирита и пиротина. Рутил показује фина прорастања са серицитом и зонарност узроковану неуобичајеним примесама волфрама до 2,2 мас.% W (сл. 3, таб. 2). Рудни минерали бакра, бизмута, олова, цинка и кобалта, који образују карактеристична међусобна прорастања и издвајања, образовани су истовремено, а заједно с њима депоновани су и кварц и анкерит, као пратећи минерали. Рутил и серицит су образовани у наредној парагенетској сукцесији истог стадијума минерализације. На тај начин, може се закључити да је испитивана минерална парагенеза образована у високо- до средњотемпературном хидротермалном стадијуму из једног веома комплексог флуида обогаћеног Cu-Bi-Fe-Pb-Zn-Ag-Co-Ni-Ti-W-As-Sb-S-Te асоцијацијом метала.

Ова минерализација је вероватно генетски повезана с горњанским гранитоидом. Међутим, с обзиром да је откривена у метаморфитима који се јављају близу контакта с гранитоидом, не постоји непосредна просторна веза минерализације с гранитоидским масивом. Из тог разлога, треба узети у разматрање и могућност генетске повезаности минерализације са филитима из метаморфне основе.

Полиметалична минерализација откривена у Перином потоку представља, према сазнањима аутора, прву појаву оваквог типа Cu-Bi-(Pb-Zn-Co-Ag) минерализације у североисточној Србији. Овакав тип минерализације може бити и економски интересантан, посебно ако се има у виду који су све метали присутни у асоцијацији (Cu, Bi, Pb, Zn, Ag, Co, итд.). Овај тип минерализације може имати и значајан допринос металогенези овог рудоносног дела Србије, у којем се јављају бројне Au, W, Mo и друге полиметаличне рудне жице у варисцијским гранитоидима и метаморфној основи у којима се ови гранитоидни масиви налазе. Даљим испитивањима ове минерализације у Перином потоку и осталих појава које се јављају на сличан начин у овом делу Србије, требало би јасно установити њихову генетску повезаност са варисцијским гранитима и/или околним метаморфитима.

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Pinite-cordierite from spotted slate of the Brajkovac contact metamorphic aureole (Dudovica locality, central Serbia)

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Abstract. The Paleozoic very low to low-grade metamorphic rocks of the Bukulja-Lazarevac Unit designated as Drina, Golija and Birač formations are contact metamorphosed by the intrusion of the Tertiary Brajkovac granodiorite into spotted slates and hornfelses. In some parts, they are slightly migmatized at the contact. In addition to their outcrops found at the western, eastern and northern parts of the formation, these rocks are also found in boreholes near Dudovica at about 8 km south-west from the pluton. There, at a depth of 110 m, the spotted slates comprise oval to ellipsoid pinite-rich spots which can be regarded as incipient cordierite porphyroblasts (up to 5 mm in diameter) overgrowing the existing regional foliation. They are composed of cryptocrystalline mixture of a very fine sericitic material ± light glassy orange „film" (some kind of an amorphous gel-like material often mixed with limonite matter) and are abundant in inclusions: minute quartz and dusty ore minerals (magnetite) prevail. In addition, within some spots an increased number of xenotime and monazite inclusions are noted. Minute flakes of neobiotite are formed at the expense of quartz-sericite-chlorite matrix. The secondary chlorite occurring as overgrowths on pinite-cordierite spots shows variable composition (brunsvigite to diabandite). The Mg/Fe+Mg ratio of cryptocrystalline pinitic mixture ranges from 0.14–0.67. The Si vs $Al^{IV}+Al^{VI}$ relations deviate from the ideal muscovite-phengite join due to Tschermak substitution towards chloritic composition or a more complex mixture, including clay minerals (which reflected a decrease of Al_{tot} and Si with increase of Fe^{2+}). Obtained data indicates that the cordierite-pinite spots can be related to contact metamorphic processes that occurred within the temperature range 300–450 °C.

Key words: granodiorite, contact aureole, spotted schist, pinite-cordierite, central Serbia.

Апстракт. Источно од Јадарског Блока, на потезу између Аранђеловца и Лазаревца, издвојена је због врло сложене грађе геотектонска јединица Букуља–Лазаревац која се састоји од врло ниско до ниско метаморфисаних стена палеозојске старости међу којима је, на основу литолошких и структурних карактеристика, издвојено неколико мањих суб-јединица или формација. Под утицајем Брајковачког гранодиоритског тела, утиснутог током терцијера, формације Дрина, Голија и Бирач су контактно метаморфисане у слејтове и различите типове хорнфелса. На непосредном контакту уочене су и врло уске зоне слабе мигматизације (до 1 m). Осим на површини, контактно метаморфни продукти тј. бобичави шкриљци са пинитизираним порфиробластима кордијерита су откривени у језгрима истражних бушотина у подручју Дудовице (око 8 km од Брајковца) на дубини од 110 m. Овални до елипсоидни појкилобласти, у различитом степену пинитисаног кордијерита, величине су до 5 mm. Развијени су на постојећем слабо рекристалисалом и контактно метаморфисаном кварц-серицит-хлоритском (± необиотит) матриксу уклапајући га и не ремeтећи примарни фолијативни склоп стене. Осим уклопака минерала основе садрже ситне љуспе необиотита, а некад и у већем броју инклузије ксенотима и

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монацита. Пинитске партије у њима састоје се од криптокристаласте мешавине серицитског материјала и стакласте изотропне геласте материје измешане са финодиспергованим лимонитом. У неким порфиробластима уочена су и секундарна нарастања хлорита (брусвингит-диабандит) по пиниту. Криптокристаласте пинитске партије имају Mg/Fe+Mg однос између 0.14–0.67. Однос Si и $Al^{IV}+Al^{VI}$ одступа од идеалног мусковит-фенгит пара и чермакитске супституције ка више хлоритским саставима или чак ка комплексијим мешавинама укључујући и минерале глина: одражава се опадањем Al_{tot} и Si са растом Fe^{2+}. Добијени подаци показују да су пинит-кордијеритски бобичави шкриљци формирани у температурном опсегу између 300–450 °C.

Кључне речи: гранодиорит, контактни ореол, бобичави шкриљац, пинит-кордијерит, централна Србија.

Introduction

The basic feature of the majority of the outer contact metamorphic zones is the production of spotted slates formed at the expense of argillaceous rocks or their very low to low grade regionally metamorphosed products (slate/schist). Generally, the spotted texture is the result of the metamorphic reactions that take place due to heat released from the adjacent magma body: the quartz-clayish or quartz-sericite-chlorite foliated matrix becomes reactive in this condition. At certain places, the ions mobility can cause it to change into a completely new composition where mineral phases with high activation energy of nucleation (e.g. cordierite) can start to crystallize. At the beginning they will form oval spots up to a few millimeters in size and then, due to temperature increase, they turn into porphyroblasts towards the contact. According to a number of authors (e.g., Chandler 1975; Haslam 1983; Nédélec & Paqet 1981; Clemens & McMillan 1982; Ogiermann 2002; Deer *et al.* 1962; Çerny & Povondra 1967; Schenk & Armbruster 1985; Haslam 1983) the composition of these spots is still uncertain. They can represent either the very fine-grained crystalline mixture of phyllosilicates (occasionally accompanied by a light yellowish amorphous isotropic material), formed as the first product of low temperature contact metamorphic reactions (often similar to pinite), or the incipient growth of cordierite. Moreover, there is a doubt whether these pinite-like spots are formed as prograde metamorphic phases or as retrograde products of cordierite porphyroblasts (see Deer *et al.* 1962; Pattison & Tracy 1991; Miyashiro 1994; Ruiz Cruz & Galan 2002; Ogiermann 2002). Also, these pinite-like spots can be composed of hydrous alkali-bearing phyllosilicates (Chandler 1975; Haslam 1983; Nédélec & Paqet 1981; Clemens & McMillan 1982; Ogiermann 2002) or mixture of chlorite + muscovite ± clay minerals (Deer *et al.* 1962) or clay mineral-bearing assemblages and isotropic alteration products (Çerny & Povondra 1967; Schenk & Armbruster 1985; Haslam 1983). In addition, it is still uncertain at which P-T-X conditions begin the transformation of cordierite to pinite and whether it is controlled by local fluid-involved reactions.

The focus of this study is to present petrographic characteristics of spotted slates first found in the contact metamorphic aureole of the Brajkovac granodiorite during exploratory drilling at a depth of 110 m in the area of Dudovica (Fig. 1). For this study, we used a combination of macroscopic, microscopic, and SEM data, as well as microprobe major-element mineral analyses to infer the composition and origin of the pinite-cordierite spots. Mineral abbreviations used in this paper follow those recommended by Kretz (1983).

Geological setting and background

South of the Pannonian basin, within the nothern part of the western branch of the complex Vardar suture zone (see Robertson *et al.* 2009, and references therein), a few Oligocene-Miocene granitic bodies (Cer, Brajkovac, Bukulja) make a NW–SE oriented belt (see Knežević *et al.* 1994). These 30–25 to 20 Ma old granites (Knežević *et al.* 1994; Cvetković *et al.* 2007) are intruded into a smaller Paleozoic continental block-unit termed Bukulja–Lazarevac (see Trivić *et al.* 2010) which is built of fragments detached from the Drina–Ivanjica (DIU) and Jadar block (JBU) continental units associated with the Vardar suture (Karamata & Krstić 1996; Dimitrijević 2001; Karamata 2006; Hrvatović & Pamić 2005).

The Bukulja–Lazarevac unit that extends east of the JBU consists of four sub-units or formations (Trivić *et al.*, 2010): Drina (DF), Golija (GF), Kovilje Conglomerate (KC) and Birač (BF) (Fig. 1A). The 900 m thick series of very low to low grade metamorphics (metasandstone, slate, sericite-chlorite schist, greenschist, muscovite-biotite schist) of the DF represents the lowermost part of Bukulja–Lazarevac Paleozoic Unit. The ~530 m thick GF overlains the DF and mostly comprises slightly metamorphosed argillaceous to arenitic rocks with intercalations of shales and siltstone. The most widespread BF consists of fine- to medium-grained arenites interlayered with shales and siltstone. All these units underwent at least two ductile and one brittle phase of deformation referred as D1, D2 and D3 (see Trivić *et al.* 2010; Marović *et al.* 2007): D1 is recorded by small-scale isoclinals and oblique folds and D2 by m- to dm-sized folds formed

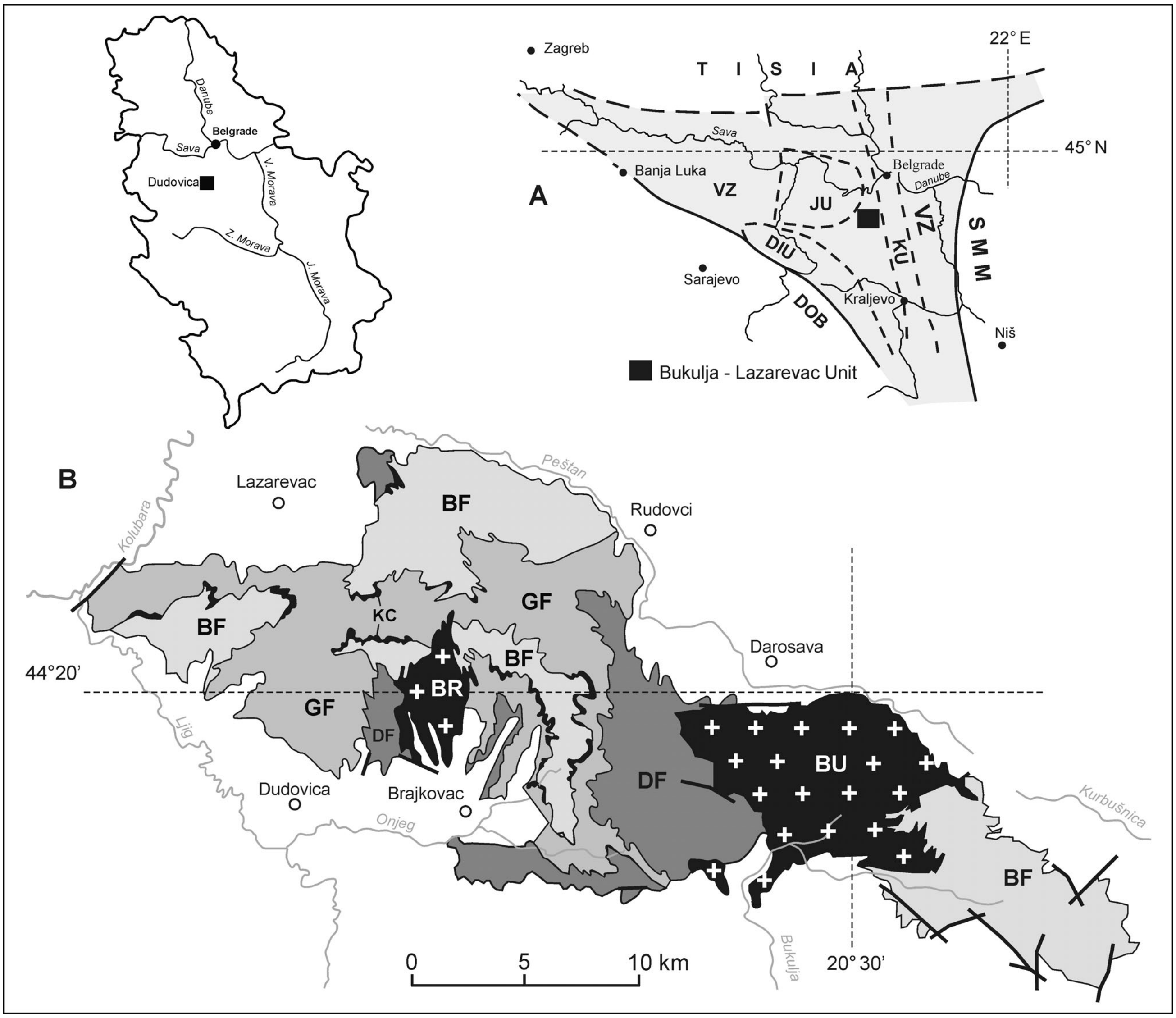

Fig. 1. Geographic position of Dudovica locality in Serbia; **A,** Position of Paleozoic tectonic units within Vardar Zone suture (according to Karamata, 2006 and Robertson *et al.* 2009); **B,** Geological position of the Paleozoic sub-units - formations and Tertiary granitoid bodies within the Bukulja–Lazarevac Paleozoic Unit (according to Trivić *et al.* 2010). Abbreviations: **VZ,** Vardar Zone; **JU,** Jadar Unit; **DIU,** Drina–Ivanjica Unit; **KU,** Kopaonik Unit; **DOB,** Dinaride Ophiolite Belt; **SMM,** Serbo-Macedonian Massive; **DF,** Drina Formation; **GF,** Golija Formation; **KC,** Kovilje Conglomerates; **BF,** Birač Formation; **BR,** Brajkovac granodiorite; **BU,** Bukulja granite.

on the limbs of the larger fold structures; D3 affected D1 and D3 in a brittle manner. It should be stressed out that the age of these sub-units and phases of deformations has not yet been fully resolved (see Trivić *et al.* 2010; Marović *et al*. 2007, and reference there in).

The contact metamorphic changes of various degree, took place due to the intrusion of the Brajkovac granodiorite, are recorded in the DF, GF and BF.

According to Kostić & Pavlović (1978) the effects of contact metamorphism which could be seen even at a distance of 5 to 8 km from the exposed granodiorite mass indicates the existence of a much greater undiscovered body that could be linked to the Bukulja granite. The spread of the Brajkovac granodiorite to the northeast is supported by geophysical exploration in the area between Baroševac and Rudovci (~ 5–6 km from the exposed mass) where it was found at a depth of about 80 m (Vukašinović 1970). In addition, the discovery of spotted slates in exploration boreholes at a depth of 110 m (Dudovica locality, about 8 km south of the exposed granodiorite; Srećković-Batoćanin *et al.* 2013), also points to its much wider distribution. The above mentioned authors emphasized that the contact metamorphic changes within the basement? rocks took place at moderate P–T conditions recorded in feldspatic biotite-muscovite rich hornfelses with rare porphyroblasts of andalusite adjacent to contact, and feldspatized or metasomatized muscovite-biotite schists at some distance from it. FILIPOVIĆ *et al.* (1978) and FILIPOVIĆ *et al.* (1980) also recognized various types of hornfelses, sericite ± chlorite or biotite-muscovite schist (± andalusite) and feldspatized or metasomatized schists, at similar distance from the contact; data related to the conditions of contact metamorphism are lacking.

The Brajkovac granodiorite is not well studied yet. The available data on its composition and associated contact aureole are very scarce as can be seen from the previous discussion. It is classified as medium- to fine-grained, rarely porphyritic, hornblende-biotite granodiorite with local transition to tonalite (KOSTIĆ & PAVLOVIĆ 1978; FILIPOVIĆ *et al.* 1980; KNEŽEVIĆ *et al.* 1994). Small intrusions of aplitic granite and very rare aplite and pegmatite dykes are also noted. The main rock-type is granodiorite and is composed of quartz, plagioclase (32–38 % An), microcline, biotite and hornblende; accessories are epidote, allanite, titanite, apatite, zircon and Fe-Ti oxides; secondary minerals are calcite, chlorite, sericite and epidote.

Analytical techniques

The samples were examined in thin sections using a Leica DMLSP petrographic microscope with digital camera Leica DC 300. Chemical compositions of mineral phases were identified using a JEOL JSM-6610LV Scanning Electron Microscope that was connected to an X-Max Energy Dispersive Spectrometer. The samples were covered with carbon using a BALTEC-SCD-005 Sputter coating device, and the results were recorded under high vacuum conditions, with an accelerating voltage of 20 kV and a beam current of 0.5–1.8 nA. The scanning electron microscope is also used for imaging of specimens.

Results

The contact metamorphic rocks found at a depth of 110 m in the drillhole at Dudovica locality correspond to porphyroblast-bearing spotted slates (Fig. 2) formed under the influence of Brajkovac granodiorite (30–25 Ma) on low grade regionally metamorphosed argilaceous sediments of Paleozoic age. Their primary metamorphic fabric is completely preserved. The main mineral assemblage is quartz, muscovite (sericite), chlorite, biotite and cordierite-pinite; dusty ore minerals (magnetite), xenotime and monazite are accesories; secondary chlorite is also present. The grain sizes of foliated matrix minerals (white mica +quartz + chlorite ± neobiotite + dusty ores) range from <0.01 mm to 0.15 mm. Cordierite, occurring in oval to ellipsoidal poikilobalsts up to 5 mm in diameter, contains numerous inclusion of matrix minerals (white mica + quartz) ± neobiotite. Within all examined samples cordierite is almost completely altered to a bright yellowish pinite – a mixture of very tiny white micas, chlorite and probably clay minerals. Within some poikiloblasts a small accumulation (up to 0.25 mm) of secondary chlorite was found as overgrowths on pinite (Fig. 2A) Moreover, some porphyroblast are transformed into a bright orange-brown vitreus isotropic material probably formed as a weathering product. The relationships between cordierite poikiloblasts and regional foliation indicate their post-tectonic growth with respect to the Paleozoic (post-Variscan) deformation, i.e. cleavage (Fig. 2 A, B). Quartz, except as matrix mineral, makes small lens-shaped fine-grained mosaic aggregates parallel to schistosity. Biotite occurs in light brown flakes (< 0.3 mm in size) associated with matrix white micas (sericite–phengite) and chlorite. It is also found as inclusion

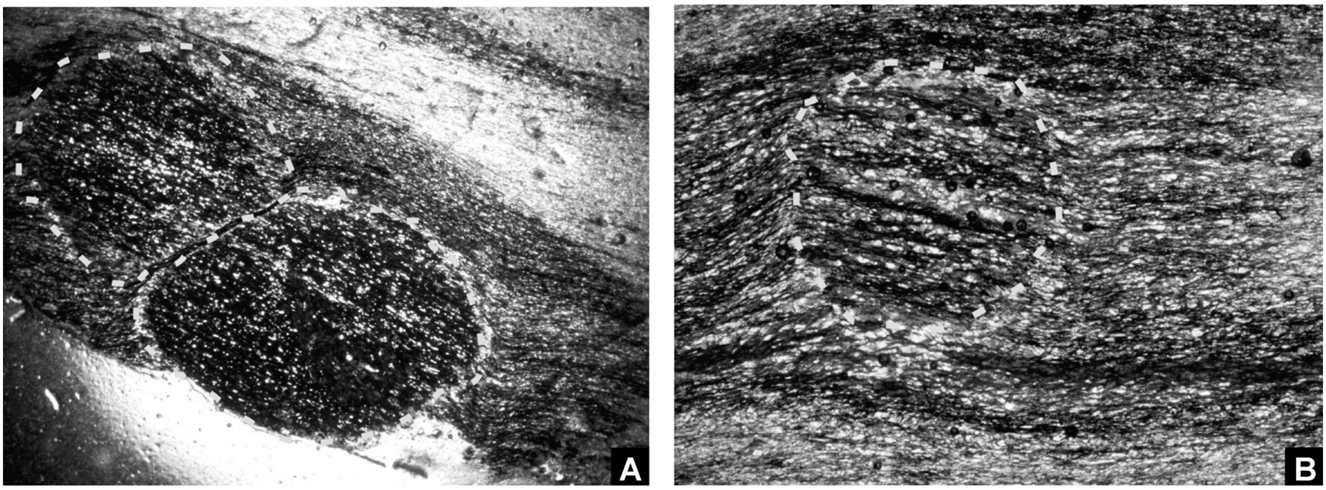

Fig. 2. Microphotographs of spotted slate from the core drilling at the depth interval of 108–110 m. **A,** Pinitized incipient cordierite poikiloblasts overgrowing pre-existing foliated quartz-sericite-chorite-biotite matrix with secondary chlorite overgrowths; **B,** Fine flakes of neobiotite formed at the expense of quartz-sericite-chlorite matrix; cordierite poikiloblast overgrowing the existing crenulated foliation; XPL, long dimension of photo is 6 mm (A) and 3 mm (B).

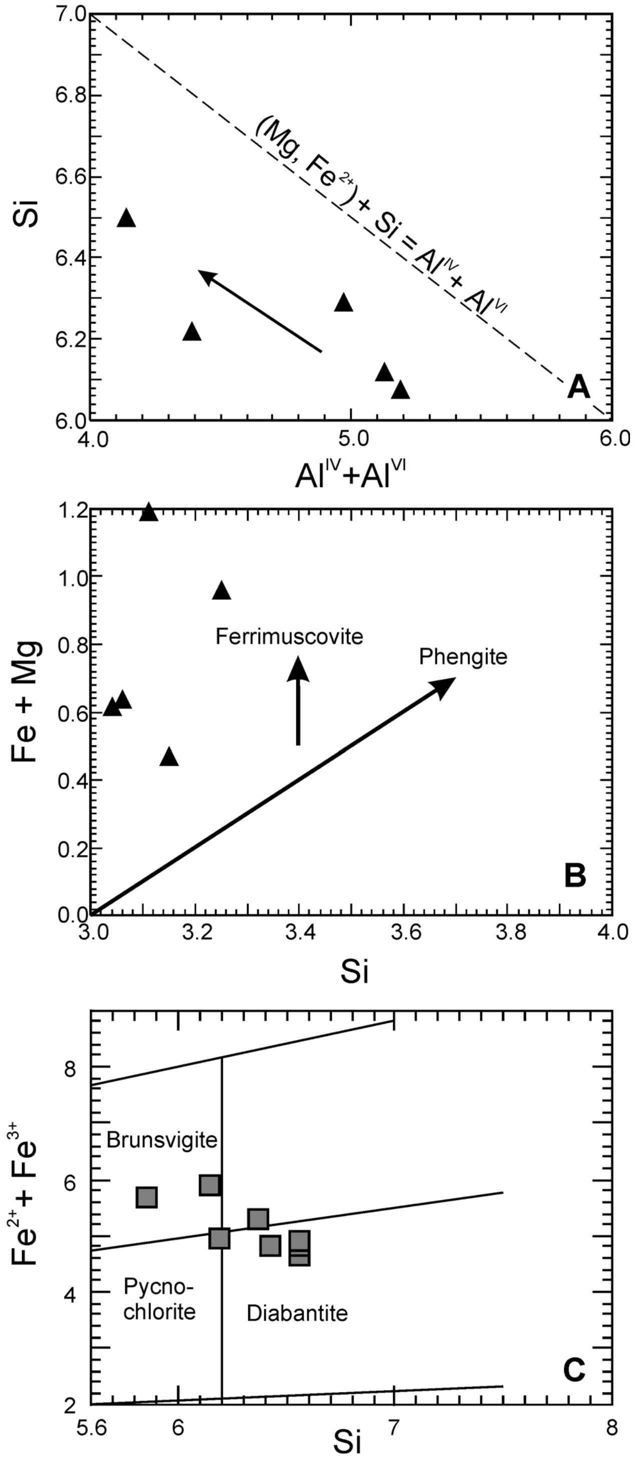

Fig. 3. Chemical composition of pinitic mixture phases in Si *vs.* Al^{IV}+Al^{VI} (A) and Fe+Mg *vs.* Si (B) diagram; (C) composition of secondary chlorite overgrowths on pinitized cordierite poikiloblasts in the classification diagram of Hey (1954).

in cordierite. Coarse calcite grains (up to 1 mm in size) are noted in some samples.

For the purpose of the present work only pinitized cordierite poikiloblasts and secondary chlorite overgrowths on pinite were analyzed; the results of the chemical analyses are shown in Table 1.

Pinite as a cordierite breakdown product is almost represented by a mixture of hydrous phyllosilicates i.e. phengite + chlorite + clay mineral phases (smectite?). The mixture of chlorite-white mica pinite is a known assemblage (e.g. Deer *et al.* 1962). The involvement of clay minerals is also reported (e.g. Çerny & Povondra 1967).

Generally, the Mg/Fe+Mg ratio of the micro- to crypto-crystalline pinitic mixture (phengite prevails) ranges from 0.14 to 0.63. The Na-free mixture (see analyses S2 & S3) with the Mg/Fe+Mg range of 0.27–0.35 shows deficiens in Al$_{tot}$ (4.14–4.38 p.f.u.) as compared with mixture having Na (0.287–0.361 p.f.u.) – there Al$_{tot}$ range varies between 4.97–5.19 p.f.u. The Si vs Al^{IV}+Al^{VI} relations deviate from the ideal muscovite-phengite join due to Tschermak substitution towards chloritic composition or more complex mixture including clay minerals which is reflected in the decrease of Al$_{tot}$ and Si with increase of Fe^{2+} (Fig. 3A, B). The K content varies from 1.385 to 1.759 p.f.u.

The secondary chlorite overgrowths on pinite correspond to brunsvigite-diabandite (Fig. 3C, 4). The Mg/Mg+Fe ranges from 0.34 to 0.43.

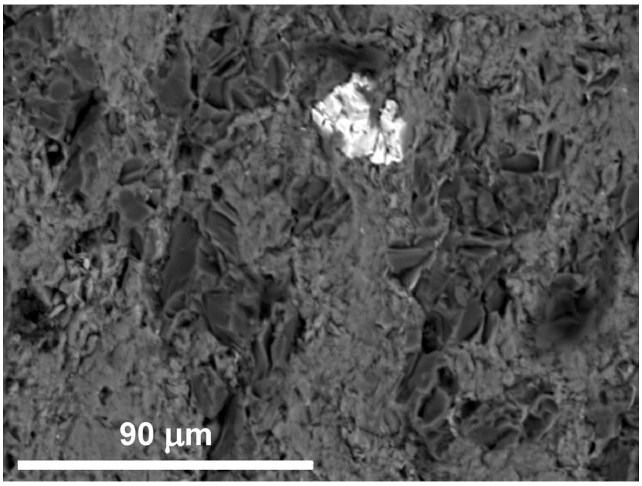

Fig. 4. BSE image of secondary chlorite overgrowths on pinitized cordierite poikiloblast and anhedral monazite crystal (white).

Disscusion and Conclusions

In exploration boreholes, at a depth of 110 m, pinite-cordierite spotted slates were found at Dudovica locality, about 8 km south of the Brajkovac granodiorite. Mineral assemblage (white mica + neobiotite + cordierite ± chlorite) and textural features indicate that these rocks were formed probably from low regionally metamorphosed argillaceous rocks of the DF in the temperature range 350–450 °C.

Pinite fractions within cordierite porphyroblast are composed of micro- to cripto-crystalline mixtures of

Table 1. Representative microprobe analyses of secondary chlorite and mixture phases from pinitized cordierite poikiloblasts.

No of analysis	Chlorite									Mixture phase spectrum				
	1	2	3	4	5	6	7	8	9	S1	S2	S3	S4	S5
SiO_2	31.51	28.00	27.07	31.37	30.23	30.08	31.82	29.69	31.01	43.85	46.37	44.38	46.36	44.29
TiO_2	0.00	0.93	0.00	0.00	0.00	0.00	0.00	0.43	0.00	0.00	0.62	0.00	0.00	0.00
Al_2O_3	17.87	16.10	18.07	19.07	17.44	18.39	16.75	18.16	18.66	31.79	25.06	26.58	31.08	31.50
FeO	26.61	32.07	31.43	27.67	29.95	26.86	28.52	28.45	27.89	8.71	11.31	12.53	2.93	8.03
MnO	0.45	0.48	0.54	0.43	0.47	0.46	0.44	0.47	0.51	-	-	-	-	-
MgO	10.83	9.43	10.24	8.94	10.45	11.39	11.85	11.43	10.40	0.83	2.40	3.82	2.79	1.43
CaO	0.79	0.30	0.38	0.36	0.00	0.75	0.46	0.74	0.78	-	-	-	-	-
Na_2O	-	-	-	-	-	-	-	-	-	1.07	0.00	0.00	1.37	1.14
K_2O	0.34	0.26	1.46	0.54	0.78	0.41	0.47	0.00	0.00	8.31	9.27	7.91	10.16	7.86
Total	88.40	87.57	89.22	88.38	89.32	88.34	90.31	89.37	89.25	94.56	95.03	95.22	94.69	94.25
	Based on 28 (O)									Based on 22 (O)				
Si	6.562	6.142	5.856	6.554	6.373	6.373	6.554	6.195	6.426	6.076	6.500	6.220	6.292	6.119
Al^{IV}	2.944	2.301	2.495	3.246	2.703	2.703	1.446	1.805	1.574	1.924	1.500	1.780	1.708	1.881
Sum_T	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Al^{VI}	2.944	2.301	2.459	3.246	2.703	2.703	2.617	2.659	2.980	3.264	2.637	2.607	3.260	3.244
Ti	-	0.153	-	-	-	-	-	0.068	-		0.065			
Fe^{2+}	4.634	5.883	5.686	4.834	5.280	5.280	4.913	4.966	4.834	1.009	1.326	1.469	0.333	0.928
Mn	0.079	0.089	0.099	0.076	0.084	0.084	0.077	0.083	0.090	-	-	-	-	-
Mg	3.362	3.084	3.302	2.784	3.284	3.284	3.639	3.557	3.213	0.171	0.502	0.798	0.565	0.295
Ca	0.176	0.071	0.088	0.081	-	-	0.102	0.165	0.173	-	-	-	-	-
Na	-	-	-	-	-	-	-	-	-	0.287	-	-	0.361	0.305
K	0.090	0.073	0.403	0.144	0.210	0.210	0.124	-	-	1.469	1.658	1.414	1.759	1.385
Cations	19.285	19.654	20.037	19.165	19.561	19.561	19.472	19.498	19.290	14.200	14.188	14.288	14.278	14.157
Mg/Mg+Fe	0.42	0.34	0.37	0.37	0.38	0.38	0.43	0.42	0.40	0.14	0.27	0.35	0.63	0.24

phengite, chlorite, clay minerals (smectite?) and quartz as well as of some amorphous gel-like material mixed with fine limonite material. Their formation could be considered as a retrogressive process involving hydration reaction caused by fluid infiltration released during the heating of the aureole (e.g. transformation of mixed-layered clay minerals into chlorite and rearrangement of illite into sericite i. e. phengite due to coupled substitution of Si and Fe^{2+} or Mg for 2Al), or from the intrusion of the granitic body. This water with dissolved ions leached from the unstable clay and phyllosilicate minerals, or fluids released during the cooling of the granitic body can cause occurrence of various retrogressive products within the cordierites.

The brunsvigite-diabandite chlorite overgrowths on pinitized cordierite are probably formed in the temperature range 250–350 °C due to circulation of still hot hydrothermal K-bearing fluids according to the reaction:

$$\text{Crd} + K^{+} + OH^{-} + H_2O \rightarrow \text{K-bearing White Mica} + \text{Chl}$$

So far, the composition of pinite and its petrological significance has not been resolved yet. The SEM analyses done in this study are not sufficient for complete identification of pinitic phases. Detailed model reaction can only be done using more sophisticated methods as for example, TEM (Transmission Electron Microscopy), RS (Raman spectroscopy), and FTIR (Fourier Transform Infrared spectroscopy).

The first finding of pinite-cordierite spotted slates within the contact metamorphic aureole of the Brajkovac granodiorite contributes to a better understanding of granodiorite history as well as of its relationship with Paleozoic formations.

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Резиме

Пинитизирани кордијерит у бобичавим шкриљцима из контактног ореола Брајковца (Дудовица, централна Србија)

Хорнбленда-биотитски гранодиоритски масив Брајковца, са локалним прелазима ка тоналитима и леукогранитима је средњо- до ситнозрнасте, ређе порфироидне структуре. Испресецан је ретким танким жицама аплита и пегматита. Интрузијом гранодиорита Брајковца (30–25 мил. год.) стене из формација Дрина, Голија и Бирач (издвојене на основу литолошких и структурних карактеристика у оквиру геотектонске јединице Букуља–Лазаревац) контактно су метаморфисане у различите типове слејтова, бобичавих шкриљаца и хорнфелса. На непосредном контакту уочене су и врло уске зоне слабе мигматизације (до 1 m). Ефекти контактног метаморфизма уочени на удаљеностима између 5–8 km од гранодиоритског тела геофизичким испитивањима у подручју Барошевца и Рудоваца указују на постојања веће, неоткривене интрузије која је највероватније повезана са гранитом Букуље. У складу са овом претпоставком је и налазак бобичавих шкриљаца са пинитизираним порфиробластима кордијерита који су окривени у истражним бушотинама у подручју Дудовице (око 8 km јужно од Брајковца) на дубини од 110 m. Ове контактнометаморфне стене су изграђене од кварца, мусковита (серицита), хлорита, биотита и кордијерита-пинита. Прашкасти метални минерали (магнетит), ксенотим и монацит су акцесорни, а као секундарни састојци појављују се хлорит и крупнозрни калцит (до 1 mm) у виду нагомилања. Овални до елипсоидни појкилобласти (порфиробласти) кордијерита, величине до 5 mm у пречнику, у свим испитиваним узорцима замењени су пинитом (мешавином ситнољуспастог серицита , хлорита и евентуално минерала глина) у различитом степену.

Састав пинита, ако се узму у обзир расположиви литературни подаци, још увек није потпуно дефинисан. Може да се састоји од: а) врло финозрних агрегата минерала из групе филосиликата и/или аморфне оптички изотропне материје; б) хлорита, мусковита и минерала глина, као и мешавине минерала глина; ц) изотропних алтерационих продуката. Нејасно је, такође, да ли је пинит представља само фазу у развоју кордијерита у току прогресивног метаморфизма или резултат ретроградних процеса и при којим P-T-X условима почиње трансформација?

У испитиваним стенама пинит је развијен на рачун слабо рекристалисалог и контактно метаморфисаног кварц–серицит–хлоритског (± необиотит) матрикса; уклапајући га не ремети примарни фолијативни склоп стене. Осим уклопака минерала основе порфиробласти садрже и ситне љуспе необиотита, а некад и у већем броју инклузије ксенотима и монацита. Пинитске партије у њима састоје се од криптокристаласте мешавине серицитског материјала и стакласте изотропне геласте материје измешане са финодиспергованим лимонитом. У неким порфиробластима уочена су и секундарна нарастања хлорита. Криптокристаласте пинитске партије (преовлађује фенгит) имају Mg/Fe+Mg однос између 0.14–0.63. У фазама без Na (анализе S2 и S3, Табела 1) Mg/Fe+Mg однос јесте 0.27–0.35, а садржај Al_{tot} (4.14–4.38 p.f.u.), и знатно је нижи него у фазама са Na (0.287–0.361 p.f.u.). Однос Si и $Al^{IV}+Al^{VI}$ одступа од идеалног мусковит-фенгит пара и чермакитске супституције ка више хлоритским саставима или чак ка комплексијим мешавинама укључујући и минерале глина: одражава се опадањем Al_{tot} и Si са растом Fe^{2+}. Садржај калијума износи 1.385–1.759 p.f.u. Секундарни хлорит настао по пиниту одговара по саставу брусвингиту идиабандиту. Вероватно је настао на температурама 250–350 °C у фази кретања још топлих флуида богатих калијом, по следећој реакцији:

$$Crd + K^+ + OH^- + H_2O \rightarrow \text{K-лискун} + Chl$$

Добијени подаци показују да су пинит-кордијеритски бобичави шкриљци формирани у температурном опсегу између 300–450 °C на рачун слабо регионално метаморфисаних глиновитих седимената из Дрина формације. Пинитске партије у кордијериту могле су бити образоване или ослобађањем флуида у фази загревања околних стена при процесима трансформације минерала глина у хлорит или илита у серицит (фенгит) при чермакитској субституцији S или пак под утицајем флуида ослобођених при хлађењу гранодиорита Брајковца.

Важно је истаћи да је ово први налазак пинита у контактном ореолу гранодиорита Брајковца и да су добијени резултати, сходно коришћеним методама, само први корак у испитивањима која следе уз примену далеко осетљивијих метода како би се идентификовале све минералне фазе.

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Application of factor analysis in identification of dominant hydrogeochemical processes of some nitrogenous groundwater of Serbia

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Abstract. Multivariate statistical analyses are used for reducing large datasets to a smaller number of variables, which explain main hydrogeochemical processes that control water geochemistry. Factor analysis (FA) allows discovering intercorrelations inside the data matrix and grouping of similar variables, i.e. chemical parameters. In this way new variables are extracted, which are called factors, and each factor is explained by some hydrogeochemical process. Applying FA to a dataset that consists of 15 chemical parameters measured on 40 groundwater samples from Serbia, four factors were extracted, which explain 73.9% of total variance in the analyzed dataset. Interpretation of obtained factors indicated several hydrogeochemical processes: the impact of sea water intrusions and volatiles in previous geological periods, solutes diffusion from the marine clay, cation exchange and dissolution of carbonate and silicate minerals.

Key words: factor analysis, hydrogeochemical processes, groundwater, factor loadings, Serbia.

Апстракт. Мултиваријантне статистичке методе користе се у циљу свођења великог броја података на мањи број променљивих, које најбоље објашњавају доминантне хидрогеохемијске процесе одговорне за формирање састава подземних вода. Факторна анализа омогућава откривање интеркорелација унутар скупа података, тј. груписање параметара који су међусобно корелисани. На тај начин се издвајају тзв. фактори, при чему се сваки фактор објашњава одређеним хидрогеохемијским процесом. Применом факторне анализе на матрицу сачињену од 15 параметара хемијског састава одређиваних на 40 узорака подземних вода са територије Србије, издвојена су четири фактора, који објашњавају укупно 73,9% укупне варијансе података. Интерпретација добијених фактора указала је на следеће хидрогеохемијске процесе: утицај морске средине и вулканских испарења у геолошкој прошлости, истискивање везане воде из глина маринског порекла, катјонску измену и растварање карбонатних и силикатних минерала.

Кључне речи: факторна анализа, хидрогеохемијски процеси, подземне воде, факторски коефицијенти, Србија.

Introduction

Assessment of the results of chemical analyses of groundwater often involves a large number of data, rendering the interpretation and presentation of all the information available to the researcher rather challenging. Multivariate statistical methods are very useful tools in hydrogeochemical research, as they allow for the organization and simplification of large datasets. They are a significant contributor to the establishment of correlations between the analyzed chemical parameters, but also to the assessment of similarities between samples (i.e. groundwater occurrences). The goal of multivariate statistical methods is to identify the hydrogeochemical processes that govern the formation of groundwater composition. If the geological and hydrogeological characteristics of the aquifer are known, by applying these methods it is possible to determine the origin and circulation pathways of groundwater. Multivariate statistical methods are also used to define migration factors and the distribution of certain elements. They can point out certain anomalies in the chemical composition of groundwater, for example those of anthropogenic nature (Helena *et al.* 1999; Cloutier *et al.* 2008; Yidana *et al.* 2008; Suvedha *et al.* 2009).

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One of the methods often applied in hydrogeochemistry is **factor analysis (FA)**. It uncovers inter-correlations within datasets or allows for mutually-correlated variables to be grouped. The main goal of factor analysis is to isolate as few as possible new variables, which are called **factors**, in order to explain the variance of a large number of analytical data. Consequently, the purpose of this method is to reduce a large number of variables (measured chemical parameters) to the smallest possible number of factors, which are then subjected to interpretation (Drever 1997; Davis 1986; Cloutier *et al.* 2008).

Study area

In this research 40 occurrences of Serbian groundwater (Fig. 1) were analyzed and a total of 15 chemical parameters were determined for each sample (macro and micro components, temperature and pH). Analyzed groundwaters are of nitrogenous composition, with a relatively low content of carbon dioxide (in most cases < 100 mg/L CO_2). Sampled groundwaters belong to different geological formations, comprised of igneous, sedimentary and metamorphic rocks, and the majority of these groundwater occurrences are located in Inner Dinarides (14 samples), Vardar Zone (20 samples) and Serbian-Macedonian Massif (six samples). Geological, structural and hydrogeological conditions in the area of investigated groundwaters are very complex. Different types of the Proterozoic to Paleozoic crystalline schists are present, and also varieties of Paleozoic and Mesozoic sediments, granitoide intrusions and the Tertiary volcanic rocks, and also characteristic oceanic elements (Dimitrijević 1995). Analyzed groundwaters are from different types of aquifers formed in these rocks, with the predominance of fracture aquifers.

Factor analysis was applied to this dataset to identify the dominant hydrogeochemical factors and processes that lead to the formation of the groundwater composition.

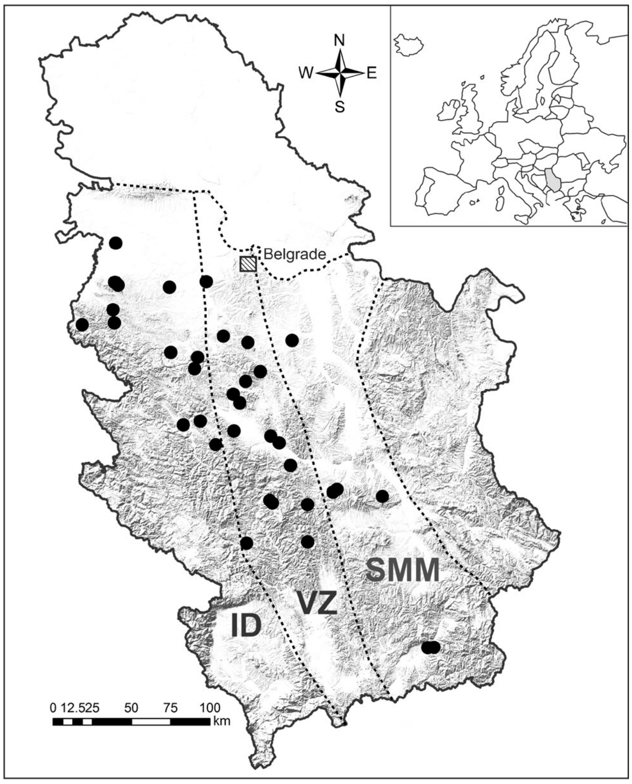

Fig. 1. Position of the study area, with the locations of analyzed groundwaters. Investigated geological-tectonic units of Serbia: **ID,** Inner Dinarides; **VZ,** Vardar Zone; **SMM,** Serbian-Macedonian masif.

Methods

Factor analysis was applied to a set of hydrogeochemical data comprised of 15 measured chemical composition parameters of 40 groundwater samples collected in Serbia. The concentrations (in mg/L) of the following elements were analyzed: calcium, magnesium, sodium, potassium, chlorine, hydrocarbonate, sulfate, silicon, fluorine, boron, lithium, strontium and carbon dioxide, as was temperature (°C) and pH. IBM SPSS Statistics 19.0 software was used for statistical analysis.

Elementary statistical quantities (arithmetic mean, minimum and maximum values, median, etc.) were determined for the analyzed set of the hydrochemical data. All the variables were subjected to ln-transformation (computation of natural logarithm of all the analyzed data). The transformed data complied with the normal distribution criterion, corroborated by the Kolmogorov-Smirnov test.

The number of the extracted factors was determined based on the Kaiser criterion (Kaiser 1960), according to which only those factors whose **eigenvalue** (characteristic value of the correlation matrix) is greater than one are taken into account. This was consistent with Cattell's scree plot, where factors constituted the X axis and their eigenvalues the Y axis. The curve was cut-off at the point of inflexion and the portion of the curve that exhibited a less steep decline was discarded (Cattell 1966). To facilitate interpretation of the extracted factors, varimax orthogonal rotation was applied to enhance the contribution of significant variables and reduce that of less significant ones (Helena *et al.* 1999; Field 2005).

Results

Based on the elementary statistical quantities shown in Table 1, it was concluded that the concentrations of most of the measured parameters did not follow normal distribution. Their distribution histograms were positively skewed, as indicated by distinctly positive coefficients of asymmetry (Table 1). For this reason ln-transformed data were used in factor analysis.

Table 1. Elementary statistical quantities for the 40 groundwater samples.

Parameters	**Minimum**	**Maximum**	**Range**	**Mean**	**Median**	**Skewness**
Temperature (°C)	13.10	83.20	70.10	28.36	21.10	1.72
pH	6.60	9.23	3.17	7.47	7.32	0.74
CO_2 (mg/L)	0.00	171.24	171.24	51.84	35.20	1.01
Ca^{2+} (mg/L)	0.00	130.26	130.26	51.21	46.89	0.48
Mg^{2+} (mg/L)	1.82	96.31	94.49	22.12	13.98	1.93
Na^+ (mg/L)	2.50	684.00	681.50	139.42	64.10	1.87
K^+ (mg/L)	0.20	51.20	51.00	5.80	2.60	3.90
Cl^- (mg/L)	2.00	223.34	221.34	44.20	21.98	2.04
HCO_3^- (mg/L)	124.44	1770.00	1645.56	504.04	400.00	2.35
So_4^{2-} (mg/L)	1.20	240.00	238.80	35.39	15.40	2.65
SiO_2 (mg/L)	9.39	91.60	82.21	32.59	25.10	1.27
F^- (mg/L)	0.05	13.00	12.95	1.62	0.70	3.12
B (mg/L)	0.00	32.60	32.60	2.02	0.29	5.09
Li^+ (mg/L)	0.003	4.78	4.777	0.31	0.10	5.21
Sr^{2+} (mg/L)	0.004	2.10	2.096	0.46	0.27	1.56

The application of factor analysis to the set of 15 variables (i.e. chemical parameters) determined for 40 groundwater samples produced four factors that together accounted for 73.9% of the total variance of the analyzed data. Table 2 shows the extracted factors, their factor loadings and the attributed percentage of the variance. **Factor loadings** represent coefficients of correlation between the variables and factors or, in other words, they indicate the relative contribution of a certain variable to each of the extracted factors (FIELD 2005). In this example, only the factor loadings whose absolute value was greater than 0.5 (bolded values in Table 2) were interpreted (STEVENS 1992). It was apparent that several variables exhibited high loadings on each factor, such that the 15 initial variables were classified into four groups, depending on their mutual similarity, to facilitate subsequent interpretation.

The first two factors accounted for nearly 50% of the variance, while the third and the fourth factors accounted for 13.3% and 11.6%, respectively. The first factor featured very high positive loadings of B, Na^+ and Cl^- (> 0.85), as well as high positive loadings of K^+, Li^+ and HCO_3^- (> 0.6). The relatively high loading of F^- (0.495) should also be noted. The second factor was characterized by high positive loadings of Ca^{2+}, Sr^{2+}, Mg^{2+}

Table 2. Factor loadings and percentage of variance explained by the four extracted factors, with varimax rotation (values in bold represent loadings with absolute values > 0.5).

Parameters	**Factor 1**	**Factor 2**	**Factor 3**	**Factor 4**
B	**0.901**	-0.190	0.085	0.045
Na^+	**0.891**	-0.270	0.164	0.158
Cl	**0.858**	0.037	0.121	-0.020
K^+	**0.687**	0.223	0.275	0.274
Li^+	**0.649**	-0.112	0.375	0.366
HCO_3	**0.632**	***0.473***	-0.430	-0.040
pH	-0.033	**-0.825**	-0.152	0.218
Ca^{2+}	-0.240	**0.808**	-0.210	-0.049
Sr^{2+}	0.207	**0.721**	0.036	0.050
Mg^{2+}	-0.260	**0.620**	-0.219	0.067
T	0.202	0.093	**0.862**	-0.025
SiO_2	0.205	-0.256	**0.742**	0.357
SO_4^2	0.191	-0.087	0.089	**0.830**
CO_2	-0.075	**0.537**	0.026	**0.579**
F	***0.495***	-0.415	0.362	**0.541**
% of variance	27.800	21.200	13.300	11.600
cumulative % of variance	27.800	49.000	62.300	**73.900**

and CO_2, as well as a high negative loading of pH, where the loading of HCO_3^- (0.473) should not be disregarded. All this is also shown in Fig. 2, where the factor loadings of all variables were plotted: the X axes represents factor 1 (left) and factor 3 (right), the Y axes represents factor 2 (left) and factor 4 (right). The variables that dominate each factor are apparent (marked by the ellipse).

The third and fourth factors accounted for the smaller portion of the variance. This was attributed to hydrogeochemical processes of a more local nature, which take place only in a certain number of groundwater occurrences (CLOUTIER *et al.* 2008). The third factor was characterized by high positive loadings of temperature and SiO_2. The fourth factor was dominated by SO_4^{2-}, but the factor loadings of CO_2 and F^- were also relatively high.

from the clays of marine origin (CLOUTIER *et al.* 2008; REIMANN & BIRKE 2010). Another possible process is cation exchange between Ca^{2+} and Mg^{2+} from the water and Na^+ from the aquifer matrix. Namely, as carbonate minerals dissolve, the groundwater becomes enriched with calcium, magnesium and hydrocarbonates, followed by the previously mentioned cation exchange, such that Ca^{2+} and Mg^{2+} concentrations in groundwater decrease while the Na concentration increases. This theory was supported by the negative factor loadings of Ca^{2+} and Mg^{2+}, and the positive factor loadings of Na^+ and HCO_3^- (GUO *et al.* 2007, CLOUTIER *et al.* 2008, SALIFU *et al.* 2011). The positive loadings for boron, potassium, lithium and fluorine of the first factor should also be noted, and they were attributed to paragenesis of these microelements and their similar hydrogeochemical behavior.

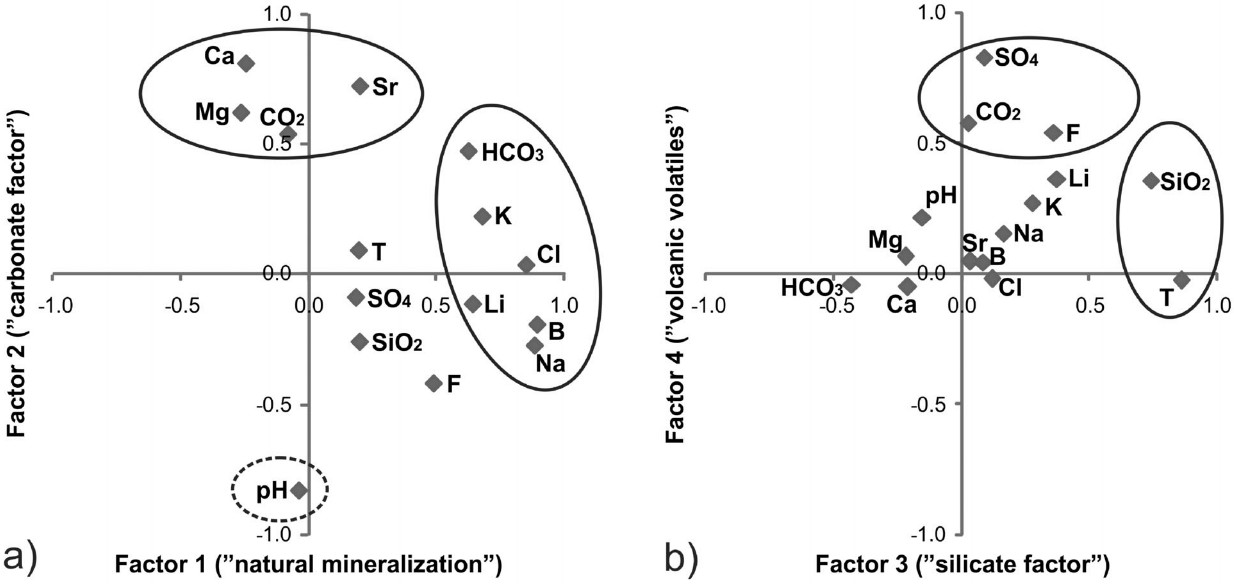

Fig. 2. Plot of factor loadings for the first and the second factors (**a**) and for the third and the fourth factors (**b**). The variables that dominate each factor are marked by the ellipse.

Discussion

If the extracted factors are viewed in a geological (primarily lithological) context, it is possible to gain insight into the main hydrogeochemical processes that lead to the formation of the chemical composition of the analyzed groundwater. In factor analysis, often all or at least the main factors are assigned conditional names, indicative of the variables that dominate the given factor. The first factor was dominated by B, Na^+, Cl^-, K^+, Li^+ and HCO_3^-, such that this factor could be called "natural mineralization" because it contains Na^+, Cl^-, K^+ and HCO_3^- that represent the ions of the basic chemical composition. Very high positive loadings of B, Na^+ and Cl^- (> 0.85) in the first factor were attributed to the groundwater mixing with seawater in the geological past, but also to the solutes diffusion

The second factor featured elevated positive loadings of Ca^{2+}, Sr^{2+}, Mg^{2+} and CO_2, and an elevated negative loading of pH. Here too, HCO_3^- needed to be taken into consideration. This factor can be called the "carbonate factor" because the dominant variables indicate the processes of dissolution of carbonate minerals. The presence of carbon-dioxide tends to render groundwater aggressive and enables the dissolution of calcite, dolomite etc., whereby Ca^{2+}, Mg^{2+} and HCO_3^- ions are released into the groundwater. This is consistent with the high positive loadings of Ca^{2+}, Mg^{2+}, CO_2 and HCO_3^-. The process takes place in an acidic environment, where the concentration of CO_2 and the pH level are inversely proportional, resulting in a negative factor loading of pH. The high positive factor loading of strontium was attributed to its paragenesis with Ca^{2+}. These two elements are chemically similar and Sr^{2+} is therefore a frequent ingredient of Ca^{2+} minerals (Hitchon 1999).

The third factor highlighted the loadings of temperature and SiO_2, attributed to the fact that the solubility of silicate minerals increases with increasing temperature (Matthess 1981), such that this factor could be called the "silicate factor". The fourth factor featured elevated loadings of SO_4^{2-}, CO_2 and F^-. This association is indicative of the volatiles from volcanic activity in the geological past and the factor was given the name "volcanic volatiles".

Conclusions

Factor analysis is an efficient tool for assessing hydrogeochemical data because of the high data variance caused by a series of geological, hydrogeological and other factors. It enables the identification of the correlations between the analyzed chemical parameters and also their grouping into factors based on similarity, which facilitates subsequent interpretation. In the present case study, factor analysis was applied to extract four dominant factors that accounted for most of the variance (73.9%) of the input dataset, which consisted of 15 chemical parameters measured on 40 groundwater samples from Serbia. The interpretation of obtained factors has indicated several hydrogeochemical processes: the effects of a marine environment and volcanic volatiles in the geological past, the solutes diffusion from the clays of marine origin, cation exchange, and the dissolution of carbonate and silicate minerals. The results uphold the significance of multivariate statistical analysis in the determination of groundwater genesis, or of the factors and processes that govern the formation of the chemical composition of groundwater.

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Резиме

Примена факторне анализе у циљу идентификације доминантних хидрогеохемијских процеса у неким азотним подземним водама Србије

Приликом статистичке обраде хидрохемијских података значајно место заузимају мултиваријантне статистичке методе. Оне олакшавају организовање и сагледавање великог броја аналитичких података, првенствено физичко-хемијских карактеристика подземних вода, а омогућавају и кла-

сификовање испитиваних узорака вода на основу већег броја одабраних параметара. Једна од метода које се често примењују у хидрохемији и хидрогеологији уопште јесте факторна анализа. Њеном употребом идентификују се и наглашавају статистичке релације између анализираних хидрохемијских параметара, уз накнадно тумачење успостављених релација са аспекта хидрогеохемијских процеса у подземним водама.

Употреба факторне анализе у овом раду омогућила је груписање хидрохемијских параметара који су међусобно корелисани и који се могу довести у везу са одређеним факторима и процесима формирања хемијског састава подземних вода. Применом ове статистичке методе на матрицу сачињену од 15 параметара хемијског састава, одређиваних на 40 узорака подземних вода са територије Србије, издвојена су четири фактора, који заједно објашњавају 73,9 % укупне варијансе података, од чега су прва два фактора одговорна за скоро 50 % укупне варијансе. Први фактор карактерише доминација B, Na, Cl, K, Li и HCO_3, па је условно назван „природна минерализација“, док код другог фактора доминирају Ca, Sr, Mg и CO_2, па му је додељен назив „карбонатни фактор“. Трећи и четврти фактор објашњавају мањи део укупне варијансе, па се њима приписују хидрогеохемијски процеси локалног карактера, који се јављају само код одређеног броја испитиваних појава подземних вода. Трећи фактор карактеришу температура и SiO_2 („силикатни фактор“), док су код четвртог фактора изражени SO_4, CO_2 и F („испарења вулкана“).

Сагледавањем издвојених фактора у геолошком, првенствено литолошком контексту, стиче се увид у главне хидрогеохемијске процесе који су значајни за формирање хемијског састава испитиваних подземих вода. Тако су издвојени следећи процеси: утицај морске средине и вулканских испарења у геолошкој прошлости, истискивање везане воде из глина маринског порекла, катјонска измена и растварање карбонатних и силикатних минерала. Добијени разултати указују на значај употребе факторне анализе, као и мултиваријантне статистичке анализе уопште, приликом утврђивања генезе подземних вода, то јест приликом дефинисања геохемијских и хидрогеолошких услова формирања тих вода.

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Natural radioactivity of groundwater in Serbia

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Abstract. Activity concentrations of radionuclides ^{40}K, ^{228}Ra, ^{226}Ra, ^{238}U and Th^{232} and gross alpha and beta activities were analyzed in more than 100 samples of groundwater in Serbia. The highest gross alpha activity was recorded at 1.33 Bq/L (average 0.12 Bq/L), while the highest beta activity was 5.43 Bq/L (average 0.68 Bq/L). The potassium isotope ^{40}K exhibited the highest active concentration (2.6 Bq/L) and was the largest contributor to the gross natural beta activity. Among the analyzed samples, 28 were found to have elevated beta activity concentrations, of which five samples also measured elevated alpha activity. All the groundwater samples that exhibited elevated radioactivity were of the HCO_3-Na type and were genetically associated with granitic rocks. Their TDS levels and CO_2 gas concentrations were also elevated.

Key words: radioactivity, activity concentration, ^{40}K, groundwater, Serbia.

Апстракт. Концентрације радионуклида ^{40}K, ^{228}Ra, ^{226}Ra, ^{238}U и ^{232}Th, као и укупна алфа и бета активност су анализирани у више од 100 узорака подземних вода са територије Србије. Укупна алфа активност достиже максимално 1,33 Bq/L са средњом вредношћу 0,12 Bq/L. Укупна бета активност има максималну вредност од 5,43 Bq/L, са средњом вредношћу од 0.68 Bq/L. Највише концентрације активности има изотоп калијума, ^{40}K који има и највећи допринос природној бета активности. Од испитаног броја подземних вода, 28 узорака је показало повишене концентрације бета активности, а пет узорака има повишене вредности алфа активности. Све испитиване воде које се одликују повишеном радиоактивношћу су HCO_3-Na типа, и генетски су највероватније везане за гранитне стенске масе. Такође, у њима је повишен садржај CO_2 као и растворених минералних материја.

Кључне речи: радиоактивност, активне концентрације**,** ^{40}K, подземна вода, Србија.

Introduction

The discovery of radioactivity and its impacts was a turning point in the evolution of geological sciences and largely affected the development of geochemistry, including isotope geochemistry, and geochronology that plays an important role in terrestrial geology. A special discipline is environmental geology that studies the impact of human activity on the environment, as well as that of natural radioisotopes (Omaljev & Antonović 1996). Radioactivity is an important parameter of geophysical measurements in gamma prospecting, logging of natural gamma radioactivity (gamma logging) and spectral gamma logging.

Prior to the discovery of radioactivity, it was believed that the main cause and source of heat flow within the Earth was cooling of its previously heated body (Marović 2005). Apart from the heat content of the Earth immediately after formation, the radiogenic decay of the unstable isotopes of uranium (^{238}U, ^{235}U), thorium (^{232}Th), and potassium (^{40}K) provides the largest internal source of heat (Clauser 2011; Hazen *et al.* 2009). The release of heat was likely more intense in the Earth's distant past than today, because the amount of radioactive elements constantly decreases as a result of decay (Marović 2005). Uranium, thorium and ^{40}K, are no longer trapped in the planet's core, they migrated to the Earth's surface in the early stages because of the crystalline and chemical properties of the compounds into which they were incorporated (Antonović 1989).

Origin of radioactivity in nature

The main α emitting radionuclides in the natural decay series are ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Po, ^{232}Th and ^{228}Th (Turhan 2013). Positively charged parti-

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cles, helium cores or ions comprised of two protons and two neutrons, make up gross alpha activity. Gross beta activity is comprised of negatively charged particles (electrons) or, rarely, positively charged particles (positrons). Nearly all radionuclides are beta emitters, except for some of the heaviest cores, while the major β emitting radionuclides are ^{210}Pb and ^{228}Ra as well as ^{40}K (TURHAN 2013). Beta emitters are generally also gamma emitters, with the exception of some pure beta (β^-) emitters such as ^{14}C, ^{45}Ca, ^{63}Ni, ^{90}Sr, ^{106}Rh and ^{147}Pm (ICRP 1991).

Environmental radiation originates from a number of naturally occurring and man-made sources. Radioactive materials occur naturally anywhere in the environment (for example uranium, thorium and potassium) (WHO 1993).

Elements 84 through 92 on the periodic table have no stable isotopes at all and can be grouped into one of three radioactive series or families. These are the uranium-radium, uranium-actinium and thorium series. Natural radioactive series are a result of decay of three radioisotopes: ^{235}U, ^{238}U and ^{232}Th, ending with isotopes ^{206}Pb, ^{208}Pb, ^{207}Pb and ^{209}Bi (USGS, 1998). The radiation generated though the decay of these naturally-occurring radioactive isotopes is the natural radioactivity found in our environment (ICRP 1991).

The radioactivity in groundwater comes mainly from radionuclides of the natural decay chains ^{238}U and ^{232}Th, and ^{40}K in soil and bedrock. Some radionuclides can migrate easily in water, depending on the mineralogical and geochemical composition of the soil and rock, redox conditions and the residence time of ground water in the soil and bedrock, as result of the reaction of the ground water with soil and bedrock (VESTERBACKA 2007).

The territory of Serbia is rich in thermal and mineral waters. Because of the volcanic and plutonic activity in the geological past, most of the mineral or thermal water originates from these rocks (PROTIĆ 1995). Groundwater occurrences mark different regional geological-structural features and the largest number of mineral groundwater is related to the granite intrusions and volcanic rocks (MARINKOVIĆ *et al.* 2013). A major portion of uranium and thorium in igneous rocks is concentrated in accessory minerals such as zircon, sphene and apatite. Other highly radioactive minerals (e.g. monazite, alanite, pyrochlore, xenotime and thorite) are found only occasionally. In general, uranium and thorium concentrations in igneous rocks increase with increasing rock acidity. The major radioactive minerals are shown in Table 1.

Table 1. Minerals and rocks featuring radioactive elements (ANTONOVIĆ 1989).

Radioactive element	Radioactive mineral	Rock/process
Potassium	Orthoclase and microcline feldspars ($KAlSi_3O_8$)	Main ingredient of acidic rocks and pegmatites
	Muscovite ($Na_2KAl(SiO_4)_3$)	As above
	Alunite ($KAl_3(SO_4)_2(OH)_6$)	Alterations in acidic volcanites
	Sylvite, carnallite (KCl, $MgCl_2{\cdot}6H_2O$)	Deposits in salt sediments
Uranium	Uraninite (oxide of U, Pb, Ra+Th, rare earth elements)	Granites, pegmatites with Ag, Pb and Cu veins
	Carnotite ($K_2O{\cdot}2UO_3{\cdot}V_2O_5{\cdot}2H_2O$)	Sandstones
	Gummite (alteration of uraninite)	Together with uraninite
Thorium	Monazite (Th_2O + rare earth phosphates)	Granite, pegmatite, gneiss
	Thorianite ($(Th, U)O_2$)	Granite, pegmatite
	Thorite uranothorite ($ThSiO_4$+U)	Granite, pegmatite

Numerous radioactive elements and isotopes occur in natural waters: uranium, radium, radon (descendants of uranium and thorium), while thorium is virtually absent because of its low mobility in geochemical systems where groundwater reservoirs develop (DANGIĆ 1995).

Methods

Sampling

During the course of the study: Radioactivity of Groundwater in the Republic of Serbia (PAPIĆ *et al.* 2008–2011), gross alpha and beta activities and the radionuclides (^{40}K, ^{228}Ra, ^{238}U, ^{226}Ra and ^{232}Th) in more than 100 groundwater samples were analyzed and represented in this paper. Sampling was conducted applying standard closed-source methods and suitable polyethylene containers were filled with 10–15 L of water.

Determination of gross alpha/beta activity concentrations

The gross alpha and beta activities of groundwater samples and gamma spectrometry measurements of natural radionuclides (^{238}U, ^{228}Ra, ^{226}Ra, ^{40}K, ^{232}Th) have been carried out in the Institute of Occupational and Radiological Health "Dr Dragomir Karajović". The gross alpha/beta analyses were performed according to a routine procedure outlined in ISO9696 and ISO9697 (ISO 9696, 1992; ISO 9697, 1992).

The gross alpha/beta activity determination method was based on the evaporation of 3 L of the water sample under UV lamps and calcining at 550 °C to a constant mass. The mineral residue was used to prepare a thin-film test sample. Suitable-geometry measurements were made on a low level proportional counter Thermo-Eberline FHT 770T, featuring a 21% efficiency for alpha radiation and 33% for beta radiation. The instrument was calibrated using standard sources. The sample measurement time was 3600 s. The measurement results were used to determine gross alpha and beta activities of the water samples in Bq/L.

Table 2. Maximum permissible concentration (MPC), average, minimum and maximum activity concentrations of radionuclides, standard deviation and median values and gross alpha and beta activities in groundwater samples collected across Serbia.

Parameter (Bq/L)	No. of samples	MPC (Bq/L)	Average	Min	Max	Std.Deviation	Median
α	125	**0.5**	0.12	0.001	1.33	0.21	0.04
β	125	**1**	0.68	0.018	5.43	0.93	0.26
^{40}K	116	**-**	0.56	0.012	2.6	0.63	0.24
^{228}Ra	116	**0.2**	0.10	0.006	0.76	0.16	0.05
^{238}U	116	**3**	0.15	0.010	0.80	0.12	0.12
^{226}Ra	116	**0.49**	0.16	0.005	2.56	0.36	0.04
^{232}Th	47	**0.59**	0.08	0.006	0.79	0.16	0.04

Determination of radionuclide activity concentrations

The method for the determination of gamma-emitter radionuclide activity was based on the evaporation of 8–10 L of the water sample to a volume of 200 mL and quantitative transfers to polyethylene vessels. The vessels were closed and left to stand for about 40 days, to prevent radon emanation and establish a radioactive balance between members of the natural radioactive series of ^{238}U. The sample was then measured on a gamma spectrometer with a HP Ge detector, whose relative efficiency was 23%. The detector was calibrated using standard radioactive reference material, MIX-OMH-F. The duration of sample measurements was 1.3 days, depending on the concentrations present. The gamma radiation spectrum was analyzed to determine the concentrations of specific radionuclides (^{40}K, ^{228}Ra, ^{226}Ra,^{238}U and ^{232}Th) in Bq/L.

Chemical analyses were performed at the Hydrochemistry Lab of the University of Belgrade Faculty of Mining and Geology to define hydrogeochemical conditions and determine groundwater types. The following parameters were analyzed: sodium, potassium, calcium, magnesium, chlorides, hydrocarbonates, carbonates, sulfates, TDS, hardness, pH, specific conductivity and CO$_2$.

The results were statistically processed using IBM software SPSS 17.0 (Inc SPSS 2009) and graphically interpreted by ESRI ArcGIS 9.3 (ESRI 2012).

Results and discussion

Basic statistical processing, including active concentration ranges, median and standard deviation (Table 2), was conducted on the basis of 125 analyses of groundwater samples for gross alpha and beta activities and a certain number of active concentrations of radionuclides ^{40}K, ^{228}Ra, ^{238}U, ^{226}Ra and ^{232}Th.

The World Health Organization, following the recommendations of the International Commission on Radiological Protection (ICRP), has studied the radiological aspects of drinking water quality and recommended reference values for α-unstable radionuclides in drinking water of 0.5 Bq/L, and β-unstable radionuclides of 1 Bq/L (ICRP 1991; WHO 1993; Official Gazette of RS 2011). When the average and median values were compared to regulated MPC (maximum permissible concentration) levels, the groundwater samples did not exhibit elevated radioactivity. However, when the maximum values of the individual parameters were evaluated, gross alpha and beta activities and the concentrations of ^{228}Ra and ^{226}Ra were found to exceed permissible concentrations. Histograms of gross alpha and beta activities and active concentrations of the tested radionuclides were produced to determine the cumulative distributions of the analyzed parameters (Fig. 1).

The histograms of gross alpha and beta activities and active concentrations of unstable radionuclides showed that all distributions exhibited positive skewness. Only five samples measured gross alpha activity in excess of the MPC of 0.5 Bq/L, while 28 samples

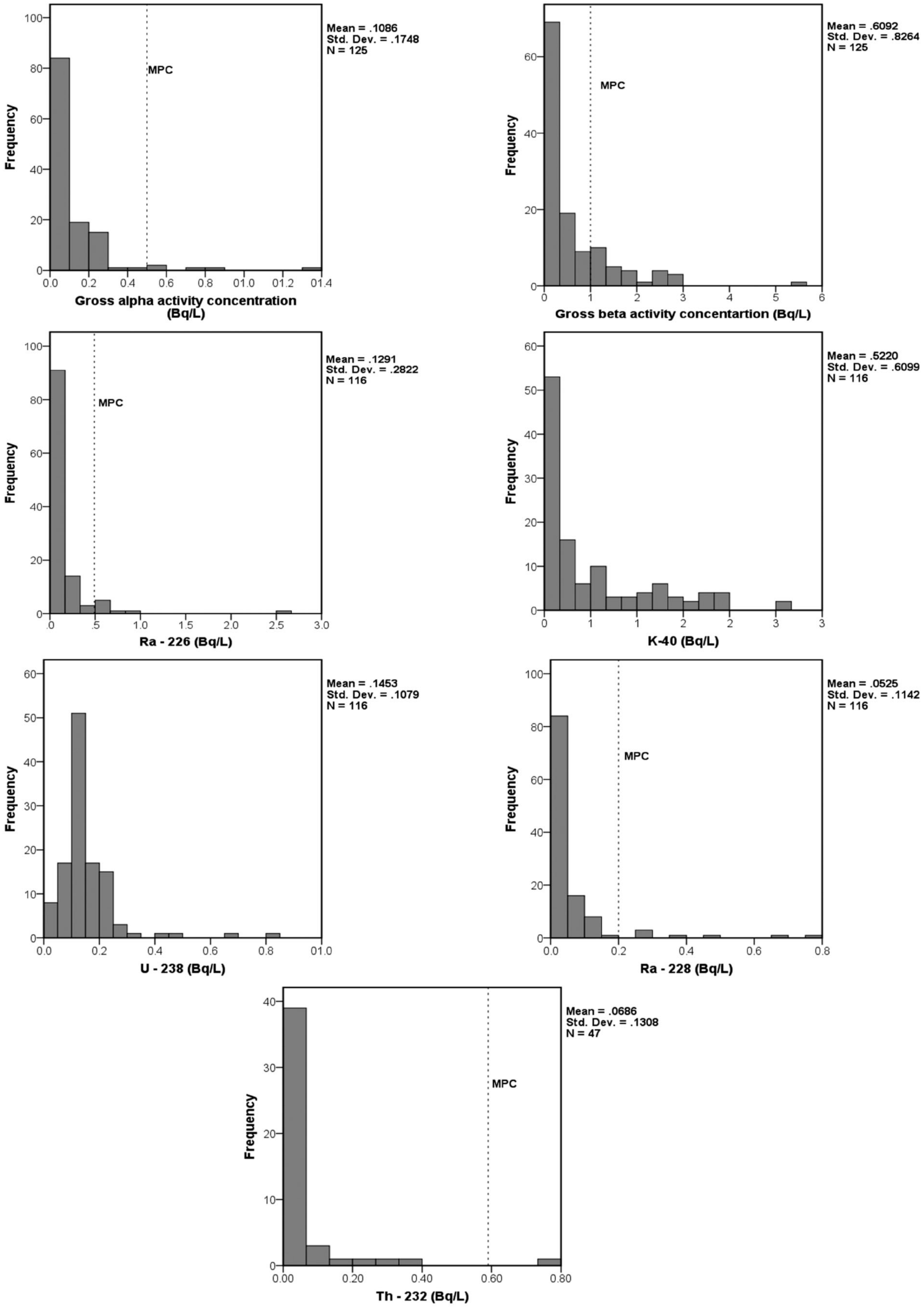

Fig. 1. Histograms of gross alpha and beta activities and active concentrations of radionuclides ^{40}K, ^{226}Ra, ^{228}Ra, ^{232}Th and ^{238}U.

were above the beta activity threshold of 1Bq/L. Radionuclides ^{226}Ra, ^{228}Ra and ^{232}Th exceeded MPC levels only in a few isolated cases, deemed to be extremes or outliers for statistical interpretation purposes and therefore disregarded. There is no regulated MPC level for ^{40}K in Serbian regulations;the average value of the samples is 0.56 Bq/L. The distribution of ^{40}K was found to be similar to that of gross beta activity and this radionuclide was the greatest contributor to gross beta activity, corroborated by high coefficient of correlation ($R^2 = 0.844$) between gross beta activity and the potassium isotope ^{40}K. The concentration of ^{40}K was found to be consistent with the geochemistry of potassium, which is one of the main elements of magma (MITTLEFELDHT 1999).

The most frequently encountered radioactive potassium minerals are orthoclase and microcline feldspars ($KAlSi_3O_8$) and muscovite ($Na_2KAl(SiO_4)_3$), which are the main minerals of acidic igneous rocks and pegmatites. Alunite ($KAl_3(SO_4)_2(OH)_6$) occurs though alteration in acidic volcanites, while sylvite and carnallite (KCl, $MgCl_2{\cdot}6H_2O$) are deposits found in salt sediments (ANTONOVIĆ 1989). ^{40}K also exhibited a high coefficient of correlation ($R^2 = 0.43$) with gross alpha activity but this result was not unexpected given that the TDS levels of the tested groundwater samples were up to 6650 mg/L. These groundwaters were formed in deep hydrogeological structures. Figure 2 shows that gross active concentrations of alpha/beta emissions increased with increasing TDS.

Both correlations between α/β activity and the concentrations of TDS (Total dissolved solids) with a coefficient of R^2=0.36 for gross alpha activity (Fig. 2A) and R^2=0.42 for gross beta activity (Fig. 2B).

The samples were divided into two groups to better understand the hydrogeochemical conditions in which the groundwaters that exhibited elevated radioactivity were formed. One group was comprised of 28 groundwater samples whose active alpha or beta concentrations exceeded MPC, and the other group was made up of 97 samples that measured below MPC. Select chemical composition parameters are presented in box-plots to show the general differences between these two groups (Fig. 3).

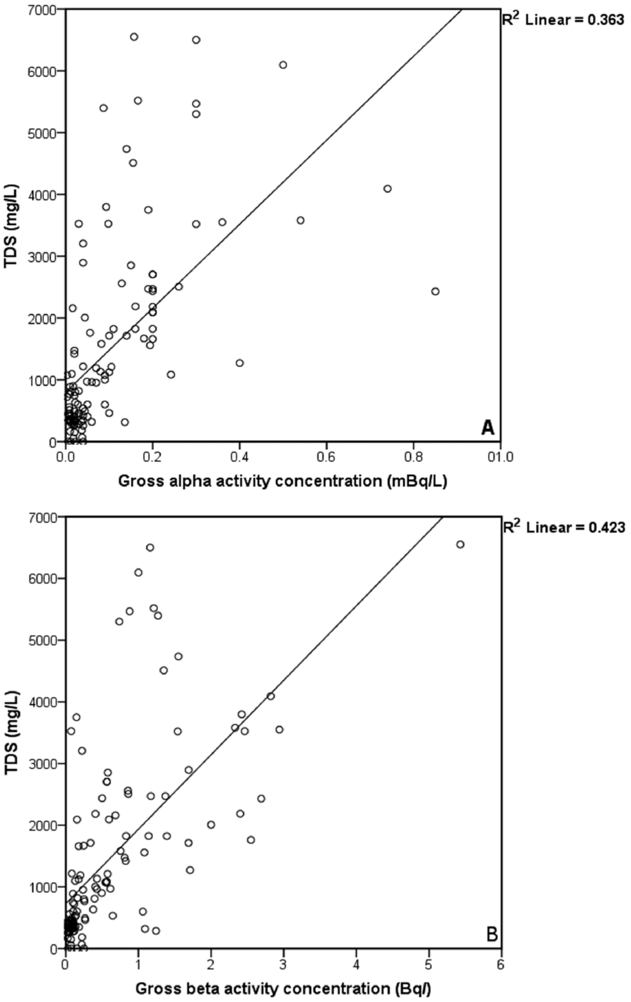

Fig. 2. **A,** Correlation between gross alpha activity and dissolved minerals. **B,** Correlation between gross beta activity and dissolved minerals.

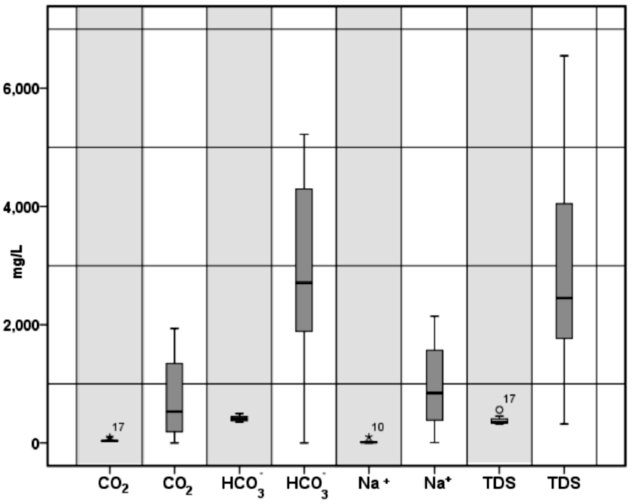

Fig. 3. Box plots of CO_2, HCO_3^- and Na^+ concentrations and TDS for two groups of groundwater samples (the group of 97 samples is shaded).

All the tested samples that exhibited elevated beta activity concentrations belonged to the Na-HCO_3 type of groundwater, suggesting that the groundwater traced to an aquifer in granitoid rocks with elevated concentrations of dissolved solids and CO_2. The samples whose radioactivity was elevated measured CO_2 concentrations up to 1510 mg/L. The water samples whose mineral content (TDS) was 500 mg/L, typical of groundwater that did not show elevated radioactivity, were dominated by Ca^{2+} and Mg^{2+} ions, while with increasing TDS these ions were replaced with the Na^+ ion.

Gas CO_2 in groundwater may be derived from a variety of sources, including metamorphic devolatilisation, magmatic degassing, oxidation of organic mat-

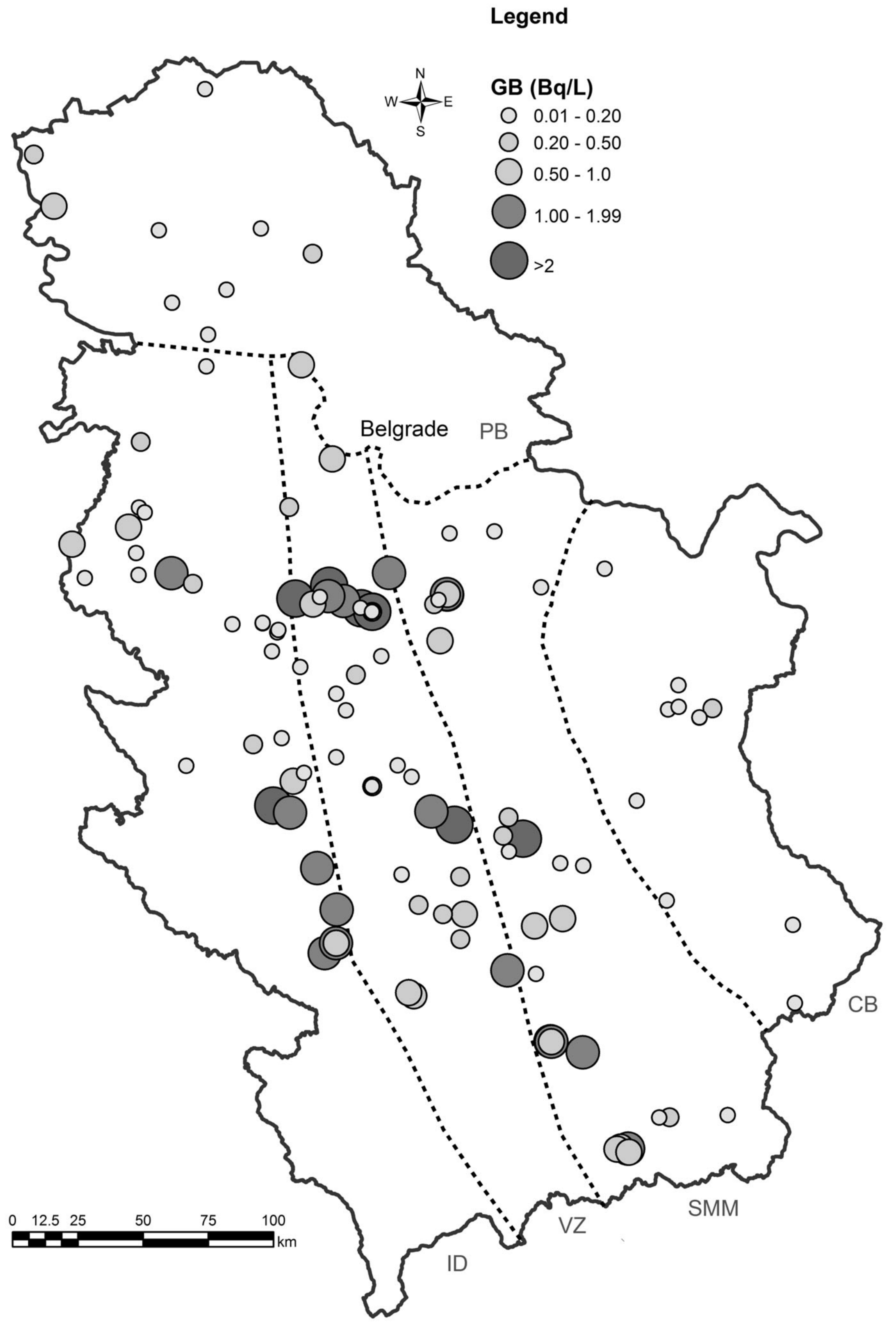

Fig. 4. Active concentrations of gross beta activity in groundwater relative to well-known geological/tectonic units. **VZ,** Vardar Zone; **SMM,** Serbo-Macedonian Massif; **ID,** Inner Dinaride; **CB,** Carpatho-Balkanides; **PB,** Pannonian Basin.

ter and interaction of water with sedimentary carbonates (CARTWRIGHT *et al.* 2001). Research conducted to date has shown that the most important radioactivity anomalies are found in calc-alkaline igneous rocks (JELENKOVIĆ 1991), which are rich in alkaline oxides and metals and make up most of the continental crust. Past studies of carbonated groundwater have shown that groundwater with elevated CO_2 concentrations tends to occur in areas of large tectonic faults, in zones of Tertiary and Quaternary volcanism and within regional metamorphism. These formation must have been related to the part of the lithosphere in which the CO_2 gas was generated. (STEVENS *et al.* 2001; MARINKOVIĆ *et al.* 2012, 2013). Spatial distribution of gross beta activity is apparent in Figure 4, and shows that most of the groundwater samples that exhibit elevated beta activity are located in the Vardar Zone or at the interface between the Vardar Zone and the Serbo-Macedonian Massif (SMM) and the Inner Dinarides (ID). This studys include 11 occurrences of groundwater from the area of the Pannonian Basin (PB) and all samples have beta activity concentrations less than 1 Bq/L. Also the area of the Carpatho-Balkanides (CB) covered by the 10 groundwater samples is characterized by low values of total beta activity.

Previous research has shown that certain deposits of radioactive elements can be spatially associated with volcanic complexes, being favorable environments for the creation of such deposits, but that the deposits themselves are linked with igneous reservoirs. It has been established that these deposits, and consequently the places where groundwater with elevated concentrations of radioactive elements is found, can occur in areas associated with large regional geotectonic zones, usually following their direction (RISTIĆ 1969). The main CO_2 generators are located within the Vardar Zone that is characterized by a highly complex geological/tectonic makeup and Tertiary magmatism and associated with the occurrence of carbonated groundwater (MARINKOVIĆ *et al.* 2012). This groundwater also exhibits naturally elevated radioactivity.

Conclusion

In this paper the distribution of natural radioactivity of groundwater from the territory of Serbia is presented, which has significant regional importance.

Determination of chemical composition and the concentration of radionuclides in groundwater may contribute in various fields within geology and hydrogeology. Gross alpha and beta activities of 125 groundwater samples collected in Serbia were determined; 28 samples featured elevated beta activity, of which 5 samples also measured elevated alpha activity. The origin of the radioactivity of these groundwater samples is natural, tracing to accessory minerals in igneous rocks. The major β-emitting radionuclide in the analyzed samples was ^{40}K, which exhibited a very high coefficient of correlation with gross beta activity. This radionuclide adheres to the geochemistry of potassium, which is one of the main magma constituents. The samples that exhibited elevated radioactivity were of the HCO_3-Na type of groundwater whose TDS exceeded 500 mg/L and CO_2 concentrations measured 33–1510 mg/L. Most groundwater occurrences that feature elevated radioactivity appear to be found in the Vardar Zone or at the interface between the Vardar Zone and adjacent zones.

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Резиме

Природна радиоактивност подземних вода у Србији

Радиоактивни елементи, потомци урана и торијума, се у великој мери јављају у природним водама. Велики део ових елемената се налази у магматским стенама и концентрисан је у пратећим (акцесорним) минералима као што су циркон, сфен и апатит. Генерално, садржај урана и торијума у магматским стенама расте са киселошћу стена. Основни радионуклиди који емитују α зрачење су ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Po, ^{232}Th и ^{228}Th, док су најважнији β радиоануклиди ^{210}Pb, ^{228}Ra као и ^{40}K.

У циљу сагледања радиоактивних особина подземних вода са територије Србије анализирано је више од 100 појава подземних вода и одређиване су концентрације радионуклида ^{40}K, ^{228}Ra, ^{226}Ra, ^{238}U и ^{232}Th, као и укупна алфа и бета активност подземних вода. Међутим, да би се разматрале радиоактивне особине подземних вода, било је потребно проучити и основни хемијски састав вода. У Лабораторији за хидрохемију, Рударско-геолошког факултета урађене су хемијске анализе ради дефинисања хидрогеохемијских услова и утврђивања типова подземних вода. Како би се утврдила веза за типом подземних вода у којој се јављају повишене концентрације радионуклида у води, одређивани су следећи хидрохемијски параметри: натријум, калијум, калцијум, магнезијум, хлориди, хидрокарбонати, сулфати, укупна минерализација, тврдоћа, pH вредност и садржај гаса CO_2. Због великог броја појава прво је приступљено утврђивању основних статистичких параметара радионуклида и алфа и бета активности (максималне, минималне концентрације, средње вредности и стандардне девијације). Од испитаног броја подземних вода, 28 узорака, је показало повишене концентрације бета активности, од чега 5 узорака има повишене вредности алфа активности. Средња вредност укупне алфа концентрације износи 0,12 Bq/L, док је за бету 0,68 Bq/L. Очигледно је да укупна бета активност представља највећим делом узрок повишене радиоактивности, а ^{40}K је радионуклид који у највећој мери доприноси укупној бета активности. Средња вредност ^{40}K износи 0,56 Bq/L.

Како би се дефинисао тип вода који се карактерише повишеном природном радиоактивношћу, сви испитивани узорци подземних вода су подељени у две групе, тако да једну групу чине воде чија укупна алфа активност прелази 0,5 Bq/L, односно укупна бета 1 Bq/L. Свих 28 појава које прелазе прописане максималне дозвољене вредности укупне алфа и бета активности припадају $Na\text{-}HCO_3$ типу воде, што указује на могућност порекла вода из аквифера који се налази у гранитоидним стенама. Уједно, ове воде се одликују повишеним садржајем растворених минералних материја и гаса CO_2. Угљен–диоксид се у узорцима са повишеном радиоактивношћу налази у опсегу 33–1510 mg/L. Подземне воде чија је минерализација мања од 500 mg/L имају доминантне јоне Ca^{2+} и Mg^{2+} (што је карактеристично за узорке који нису имали повишену радиоактивност), док се са повећањем минерализације ови јони смењују са Na^+ јонима. Самим тим се може закључити да се са повећањем растворених минералних материја у води повећава и радиоактивност подземних вода, што указује на то да се радиоактивност подземних вода везује за геолошке формације у којима су формирани аквифери.

Претходним истраживањима констатовано је да се најважније аномалије радиоактивности везују за калко-алкалне магматске стене, које чине највећи део континенталне коре, односно за области великих тектонских раседа, у зони терцијарног и квартарног вулканизма и у оквиру регионалног метаморфизма. Овим радом је представљена просторна дистрибуција укупне бета активности на територији Србије, где се уочава да је највећи број подземних вода са повишеном бета активношћу смештен у Вардарској зони или на контакту Вардарске зоне са Српско-македонском масом и Унутрашњим Динаридима.

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Rare earth elements in some bottled waters of Serbia

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Abstract. Twenty–one bottled mineral and spring waters from Serbia were analyzed for 16 inorganic chemical parameters, including lanthanides and yttrium which belong to the group of so–called rare earth elements (REE). REE concentrations in the bottled water samples varied over a broad range, from 5.39 to 1585.82 ng/L. Total concentrations in the bottled water samples were calculated taking into account the classification of lanthanides into heavy (HREE) and light (LREE), with yttrium added to the HREE group. The LREE concentrations ranged from 3.62 to 1449.63 ng/L, while those of the HREE were from 0 to 136.19 ng/L. Distinct REE signatures were observed in waters that drained specific rocks. The REE patterns in groundwater from granitic and related rocks showed LREE and HREE enrichment, while groundwater with mafic rock influence exhibited slightly LREE enrichment. Several bottled water samples featured naturally–occurring carbon dioxide, whose solutional capacity contributed to the highest REE concentrations in the analyzed samples. High REE concentrations are also a result of sudden changes in oxidation–reduction conditions, which particularly affect La, Ce and Eu. Aquifers developed in granitic and related rocks (methamorphic and sedimentary rocks) constitute favorable environments for HREE in groundwater, corroborated by the occurrence of HREE in bottled water samples. The bottled water samples largely exhibited a negative cerium anomaly and nearly all the samples showed a positive europium anomaly.

Key words: rare earth elements, hydrogeochemistry, bottled waters, Serbia.

Апстракт. Елементи ретких земаља (ЕРЗ) анализирани су у 21 узорку флашираних вода са територије Србије. Укупне концентрације ЕРЗ представљају суму тешких и лаких лантанида са итријумом, који се због сличних геохемијских особина прикључује тешким лантанидима. Концентрације ЕРЗ у узорцима флашираних вода варирају у великом опсегу од 5,39 до 1585,82 ng/L. Лаки лантаниди налазе се у концентрацијама између 3,62 и 1449,63 ng/L, док се тешки лантаниди налазе у мањим концентрацијама, од 0 до 136,19 ng/L. Издани формиране у гранитоидним и стенама на чије формирање и састав оне имају утицај, представљају средине погодне за појаву и тешких и лаких лантанида у подземним водама, док базичније стене најчешће представљају извор само лаких лантанида. Највеће укупне концентрације ЕРЗ и тешких лантанида забележене су у подземним водама у близини великих гранитоидних масива, посебно оних где се налазе појаве природног угљен–диоксида, који својим растварачким способностима доприноси бржем ослобађању ЕРЗ из стена у воду (Букуља, Бујановац). Још један узрок појаве великих концентрација ЕРЗ је и нагла промена оксидо–редукционих услова, који највећи утицај имају на La, Ce и Eu, који уједно достижу и највеће концентрације од свих ЕРЗ. Разматране флаширане воде карактерише негативна аномалија церијума док скоро све воде имају позитивну аномалију еуропијума.

Кључне речи: елементи ретких земаља, хидрогеохемија, флаширане воде, Србија.

Introduction

The mostly trivalent rare earth elements (REE) consist of group IIIb transitions elements Sc, Y and La and inner transitiion elements (or lanthanides). In geochemistry the term ‘rare earth elements’ generally refers only to the lanthanides (La–Lu). Yttrium (Y) behaves similary to the lanthanides Dy–Ho and thus is commonly included in discussions of the REE. Scandium (Sc) in contrast, is substantially smaller cation

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with distinctive geochemical behavior and thus is generally included in the ferromagnesian transition elements (Fe, V, Cr, Co and Ni) (MCLENNAN 1999). Lanthanides can conditionally be divided into three groups: light (La, Ce, Pr, Nd), medium (Sm, Eu, Gd, Tb, Dy, Ho) and heavy (Er, Tm, Yb, Lu). There is also a simpler classification, into the so–called cerium or light lanthanide group (La–Eu) and the yttrium group (Gd–Lu) comprised of heavy lanthanides and yttrium.

REE constitute a unique series of elements in nature due to their specific features that make them especially powerful tracers of fundamental geochemical processes (HANSON 1980; HENDERSON 1984). These properties derive from the fact that: (1) with the exception of Ce, the REE are generally trivalent in Earth surface systems and are thus chemically fractionated from their nearest neighbors in the Periodic Table (i.e., divalent Ba and tetravalent Hf), and (2) owing to the progressive filling of the 4f electron shell across the REE series, their ionic radii decrease with increasing atomic number (i.e., the lanthanide contraction). This lanthanide contraction imparts subtle and systematic differences in the chemical properties of REE across the series that are largely predictable, and thus highly useful in studies of those processes that fractionate REE in the environment. Consequently, the REE have a long history of use in the study of magma genesis in the Earth's upper mantle and crust, crustal evolution, and in investigating weathering, crustal denudation, transport of weathering products to the oceans, and for water–rock interactions (HANSON 1980; HENDERSON 1984; BAU 1991; SMEDLEY 1991).

Low REE concentrations in water (ppb level or less, (SHOLKOVITZ 1995 and references therein)) have long prevented their use as witnesses of water/rock interaction processes or as hydrogeological tracers. The refinement of stable isotope dilution mass–spectrometry techniques and the recent development of high–sensitivity equipments, namely the Inductively Coupled Plasma Mass Spectrometers or ICP–MS, changed this situation. As a consequence there has now been an increasing number of studies dedicated to the chemistry of dissolved REE.

A limited number of previous studies revealed that REE characteristics in groundwater systems are largely controlled by the rock through which they flow, their pH, redox conditions, solution chemistry, organic and/or inorganic complexity and the form of transport of colloidal and particulate matter. The most important finding brought out by these studies is the similarity of REE patterns between groundwater and aquifer rock. Groundwater REE signatures have been shown to reflect those of host aquifers, and are, therefore, useful tracers of flow where the mineralogy of different aquifers varies (e.g SMEDLEY 1991; JOHANNESSON *et al.* 1997; MÖLLER et al. 2003; TWEED *et al.* 2006). Many groundwaters exhibit REE patterns that closely resemble the REE patterns of the rock through which they flow, although they can show different REE patterns compared with their aquifer rock.

Understanding the geochemistry of REE in circumneutral pH terrestrial waters, such as groundwaters, is important from both the standpoint of their potential use for investigating water–rock interactions, as well as for tracing groundwater flow (MCCARTHY *et al.* 1998; JOHANNESSON *et al.* 2000). Moreover, ascertaining the behavior of the REE in natural terrestrial waters is especially significant in the study of the fate and transport of radioactive transuranics in the environment because of the chemical similarities of the REE and trivalent transuranics i.e., Pu^{3+}, Am^{3+}, Cm^{3+}, and Cf^{3+}; (CHOPPIN 1983; KRAUSKOPF 1986; MCCARTHY *et al.* 1998). Therefore, it is generally well accepted that the ubiquitous and naturally occurring REE can be used as chemical analogs for studying the behavior of the highly radioactive transuranics in natural waters.

The link between geology and water chemistry is well known and can lead to extreme differences in element distribution and is an issue that needs to be addressed. It is imortant to investigate the hydogeochemical characteristics of the waters in order to identify the main hydrogeochemical processes and influences controlling their chemical content.

Some of their unique composition features, such as elevated carbon dioxide (CO_2), hydrogen sulphide (H_2S), sulphate (SO_4^{2-}), iron and high salt content are specific to the geological and hydrogeological position of the exploited springs and producing wells. However, these naturally occurring waters are often chemically processed before bottling in order to adjust to market needs. The final bottled water product can have, therefore, little resemblance to the original groundwater composition. Nevertheless, MISUND *et al.* (1999), found a traceable link between bottled water composition and aquifer lithology in 66 European bottled waters. GROSELJ *et al.* (2008) used neural networks to arrive at the same conclusion. REIMANN & BIRKE (2010) analyzed 1785 bottled waters and and they belived that those analysis may provide a possibility to gain an idea about groundwater chemistry at the European scale. According to this study, from the aspect of rare earths, for the most elements in the group, there is no unambiguous geological explanation for high occurrences in groundwater. In general, the highest concentration of rare earth elements, from litological aspect, are related to pegmatite dyke containing REE minerals, felsic gneisses, granite and calcalkaline Tertiary volcanics (REIMANN & BIRKE 2010).

Methods

During the spring and summer of 2012, 21 bottle waters available on the Serbian market were purchased in selected shops all over Serbia. The dominant role for selection bottled water sources played their different genesis and discharge. Different conditions of water formation reflect their variations in chemical types.

In order to characterize the composition of the studied bottled waters, two data sources were used: laboratory analysis of bottled waters purchased from the public market carried out by Activation Laboratories (Canada) and the chemical composition reported on bottle labels. The physicochemical parameters reported on the manufacturer's labeling of 21 domestic brands of bottled water were used as dataset for this study. To keep the brand names anonymous, the waters were named from Brand 1 to Brand 21 and this convention was used throughout the text. The physico–chemical variables (consisting of major ions, minor ions, trace elements, and physical parameters) that were in the compiled database, seven variables (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}) occur most often and thus were utilized. Analysis of chemical and physical properties of these bottled waters were carried out by official laboratories that have been certified by the Ministry of Health and accuracy and precision of the laboratory results were not questioned in this study. However, as an independent check on the quality of the chemical analyses in the database they were tested for charge balance error using software The Geochemist's Workbench, 2008. Calculated charge balance errors are less than ±5% for all the samples in the database, which is an acceptable error for the purpose of this study. The water samples were analyzed by HR–ICP/MS, High Resolution Magnetic Sector ICP/MS using a Finnegan Mat ELEMENT 2 instrument in Activation Laboratories. In addition, to verify the accuracy and precision of the method, NIST® 1643e "Trace Elements in Water" SRM was analyzed and compared to the certified values. The experimental concentrations determined in this study agreed well with certified values.

Results and Discussion

Geological setting of rare earth elements

For the most part, REE are all lithophile and in most igneous systems they are incompatible; the degree of incompatibility increases with increasing atomic radius (or decreasing atomic number). Accordingly, lanthanides and yttrium tend to concentrate within magmatic liquids and phases that occur in the later stages of magmatic activity *(McLennan 1999)*.

Rare earth deposits in igneous rocks can be grouped into five distinct categories differing in the provenance and evolution of the magma and in the rock types hosting mineralization: (1) carbonatites, (2) peralkaline silica undersaturated rocks, (3) peralkaline granites and pegmatites, (4) pegmatites associated with sub– to metaluminous granites, and (5) Fe oxide–phosphate.

The genesis and distribution of REE during the course of differentiation of magma, magmatic remnants and hydrothermal solutions are highly complex processes, as such, they do not depend solely on tectonic zones and provinces, but on magma chemism as well acidity and alkalinity.

A large number of minerals feature complex REE compositions, light and heavy lanthanides. Depending on the magma chemism, they are divided into primary and secondary minerals. This can be seen in secondary rock constituents, largely affected by calcium and phosphorus concentrations in the early or later stages of magmatic differentiation. As a result, certain selective minerals are dominated by the cerium group: bastnaesite, parisite, loparite and monazite, while others are dominated by the yttrium series: xenotime, euxenite, gadolinite, yttrofluorite, etc. This applies to secondary rock constitutes and primary REE carriers. In addition to calcium and phosphorus, the global causes of selective REE fractioning are attributed to the general magma chemism: the Ce–group is associated with alkaline magma (basic alkaline complexes), while the yttrium group is associated with acidic magma (Arsenijević & Dromnjak 1988).

As part of the Central Balkan Peninsula, Serbia is made up of very complex geological units. Dimitrijević (1994) defined geological structure of the territory of Serbia based on geotectonical units. In general, they can be divided into the following units: Pannonian Basin, Carpatho-Balkanides, Serbian Macedonian Massif, Vardar Zones and Inner Dinarides. A simplified geotectonic framework of Serbia is presented in Fig. 1.

From an REE prospecting perspective, the research conducted to date in Serbia (Arsenijević & Dromnjak 1988) and references therein) suggests that the primary REE–carrying minerals are monazite, xenotime, alanite, apatite, fergusonite, zircon, columbite and the like. The above minerals have been detected in granitoid rocks and metamorphic rocks enveloping granite, as well as rarely in the sediments of creeks and rivers that flow through granitoid massifs. They were found in biotite and biotite–muscovite granites, aplitoid granites and granitic gneisses at the following localities in Serbia: Cer, Vršac, Bukulja, Čemerno, Željin, Bujanovac and Golija (Mihailović-Vlajić, N. & Markov, C. 1965; Petković 1987 and reference therein*)*.

Major hydrochemistry and hydrogeochemistry of rare earth elements

The differences between the chemical compositions of the bottled water samples are best seen on the

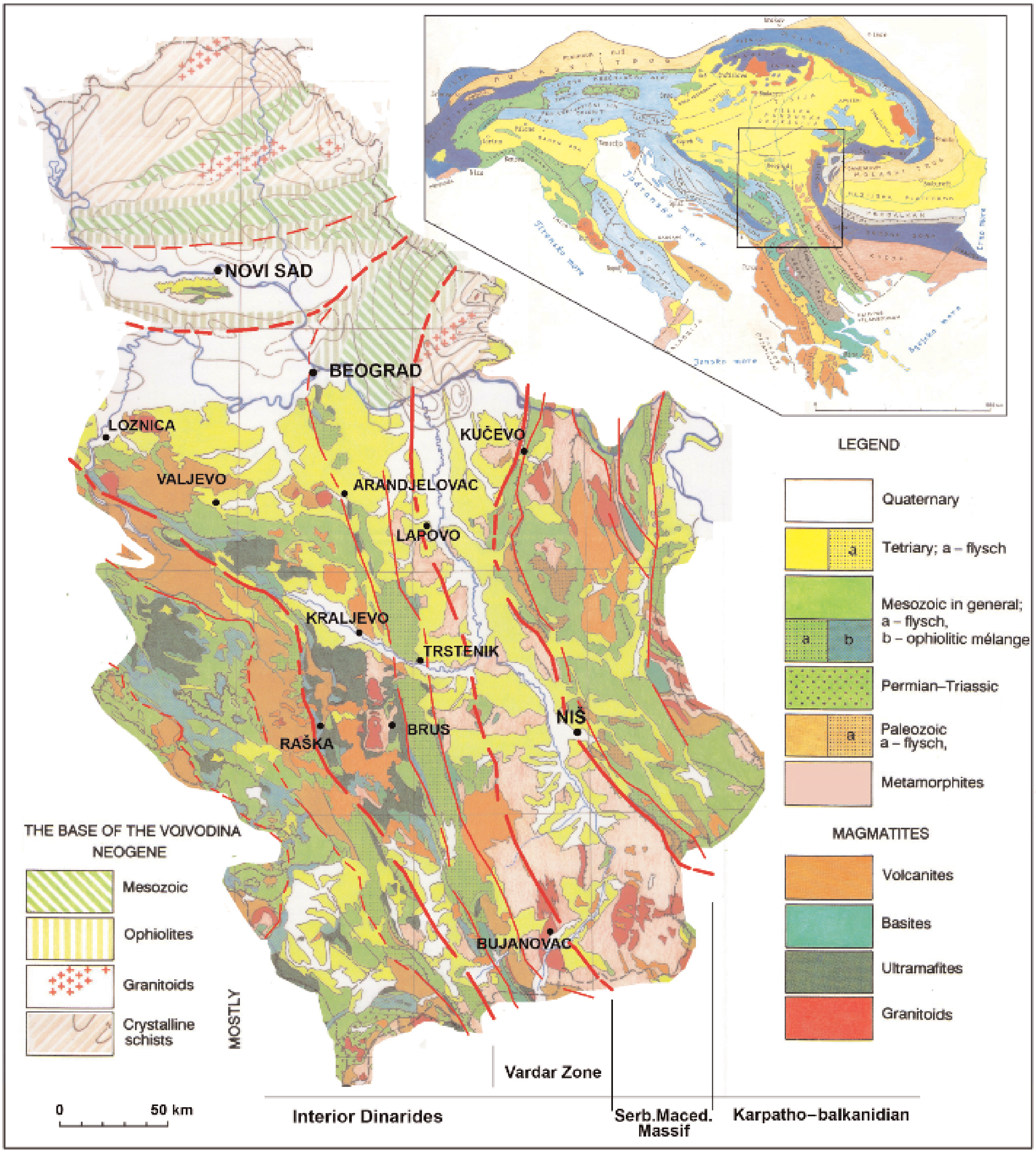

Fig. 1. Geological map of Serbia (DIMITRIJEVIĆ 1994).

Durov diagram, showing the anions, cations, TDS and pH levels in parallel (Fig. 2). The trilinear diagram of the anions shows minor differences in anionic composition; most of the bottled water samples were of the hydrocarbonate type, with only Brand 2 being of the HCO_3–Cl type and Brand 14 of the HCO_3–SO_4 type.

With regard to cationic compositions, there were two large groups: one dominated by calcium and magnesium – 7 samples HCO_3 – Ca, 2 samples HCO_3 – Mg (TDS up to 804 mg/L), and the other by Na – 12 samples HCO_3 – Na (TDS up to 3100 mg/L). No significant correlation between the macrocomponents was

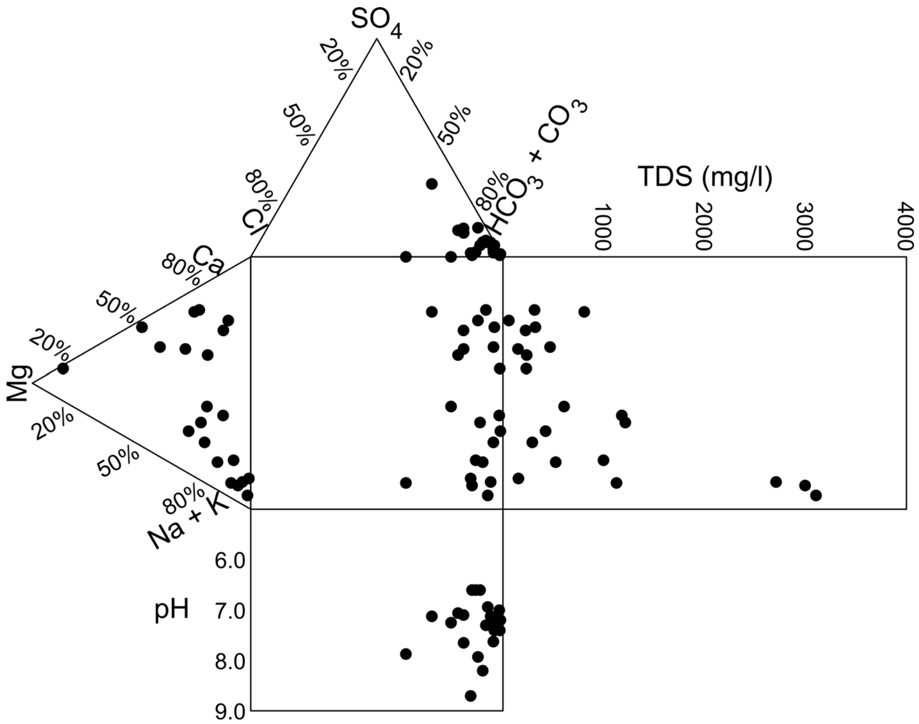

Fig. 2. Durov diagram of chemical compositions of bottled water samples.

noted, except between sodium and hydrocarbonates. Among the bottled water samples of the Na–HCO$_3$ type, 8 brands exhibited a TDS level greater than 1000 mg/L, of which 7 featured natural carbon dioxide (Brands 5, 7, 10, 15, 16, 17 and 18).

The REE concentrations in the bottled water samples are shown in Table 1 and Fig. 3, with minimum and maximum concentrations of all the members of the lanthanide group, along with yttrium and their ratios.

Table 1. Minimum and maximum REE concentrations in bottled water samples, including their ratios (ng/L).

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Min	<1	<1	<0,05	<0,1	<0,5	2,46	<0,05	<0,1	<0,5	<0,01	<0,05	<0,1	<0,05	<0,3	<3
Max	655,1	587	30,2	108,6	21,5	682,2	16,2	4,51	17,1	2,9	10,9	<5	6,02	2,8	93,1
Ratio	655,1	587	605,2	1086,9	43,0	277,4	323,1	45,1	34,2	286,9	218,4	/	120,4	9,2	31

Among the lanthanides, the highest concentrations were measured in the light lanthanide group (LREE – La, Ce, Nd and Eu). In all the samples thulium (Tm) was below the detection limit, while the highest percent concentrations below the detection limit were those of samarium (Sm) and dysprosium (Dy) (about 70%) and lanthanum (La) and cerium (Ce) (50%).

It should be noted, when compared to concentratios of rare earth elements in study of REIMANN & BIRKE (2010) one sample of bottled water exibit maximum concentration of Eu (447 ng/L) (Brand 15: 682.2 ng/L).

REE totals are shown in Fig. 4a. Brands 8, 9 and 20 exhibited the lowest summary REE concentrations, from 5.39 to 10.96 ng/L. Although no correlation was established between TDS and pH relative to the total REE, these three brands measured the lowest TDS and the highest pH levels. The chemical compositions of these bottled water samples suggested a short circulation pathway and rapid water exchange between intermediary and basic rocks. The rocks in which these waters were formed are apparently not conducive to the occurrence of REE–carrying minerals.

REE in concentrations from 23.04 to 86.6 ng/L were found in bottled water samples of different cation types and TDS levels (from Ca–HCO$_3$ to Na–HCO$_3$, Na–HCO$_3$–Cl, TDS 146–1123 mg/L). This group included waters tracing to limestones (Brands 19 and 21), marls (Brand 12), gneissic granites (Brand 4), and intergranular porosity rocks of different compositions (Brands 2, 3, 6 and 13).

Levels above 100 ng/L were recorded in bottled water samples whose chemical compositions were directly or indirectly affected by granitic intrusions and Tertiary magmatism. Similar to the previous samples, TDS did not correlate with total REE. This group included naturally carbonated waters (Brands 5, 7, 10, 15, 16, 17 and 18, Na–HCO$_3$, TDS 994–3100 mg/L), Brand 14 (Ca–HCO$_3$–SO$_4$, TDS 804 mg/L), and Brands 1 and 11 (TDS 221 and 420 mg/L). Fig.s 4b and 4c show total light lanthanides and heavy lanthanides (with yttrium), by sample.

Light lanthanides measured from 3.6 to 1449.63 ng/L. Cerium (Ce) and lanthanum (La) were the greatest contributors to these concentrations. The highest LREE concentrations were recorded in all naturally carbonated water samples (except Brand 10), as well as in Brands 1 and 14, where apart from lithology, the solutional capacity of CO$_2$ has a considerable effect. HREE concentrations ranged from 0 to 136.19 ng/L. Higher HREE concentrations were measured in samples

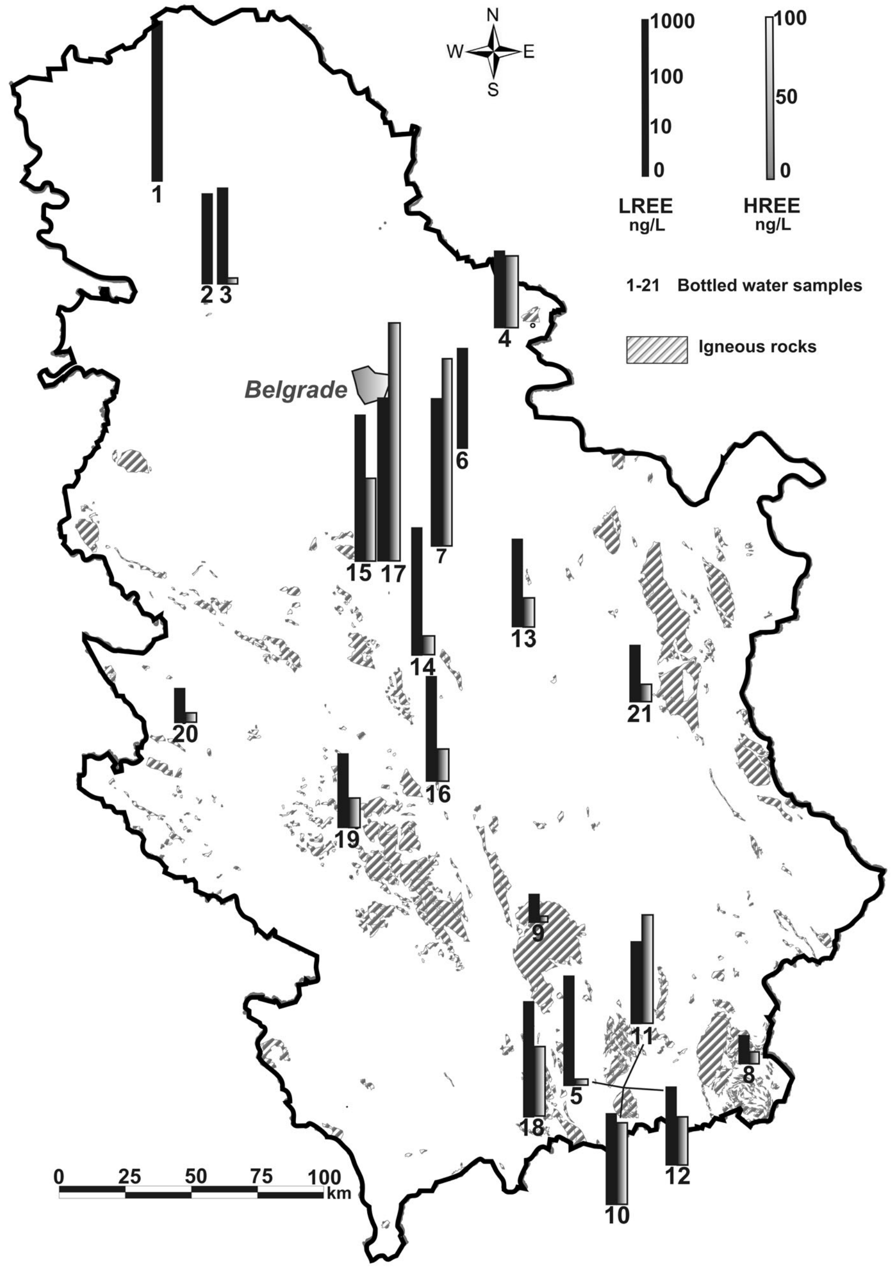

Fig. 3. Shematic map of Serbia with concentrations of LREE and HREE in analyzed bottled waters and distribution of igneous rocks.

whose composition was formed in contact with granitoid rocks, either placer deposits (Brands 7, 11, 12, 13 and 15) or circulation through the granites and related rocks (Brands 4, 10, 17 and 18). This group also included Brand 16. The groundwater used to bottle Brand 16 exhibited an elevated temperature, suggesting the influence of a granitoid intrusion on the chemical composition of groundwater formed primarily in serpentinites.

Although Brands 19 and 21 represented groundwaters tracing to limestones with low total REE, there were notable differences between both the REE totals and in terms of a higher HREE concentration in Brand 19. Additionally, the elevated temperature and the presence of heavy lanthanides in the groundwater used to bottle Brand 19 suggested a potential influence of groundwater from granitoid and metamorphic rocks on the recharge of the aquifer formed in limestones from which this water is tapped.

REE concentrations in groundwater generally depend on several factors: release into solution during the dissolution of minerals, pH levels and redox states of the groundwater, adsorption, complexing ligands in the groundwater and hydrogeological factors (e.g. flow pathways and residence time). The environmental behavior of the REE and yttrium is strongly influenced by solution chemistry (Wood 1990; Luo & Byrne 2004). In groundwater, REE are subjected to chemical complexation with several potential REE complexing agents. Trivalent REE are considered to be hard ions and will complex preferentially with hard ligands including F^-, SO_4^{2-}, CO_3^{2-}, PO_4^{3-} and OH^-. In general, simple ions (Ln^{3+}, Ln is any lanthanide) and sulfate complexes are dominant at low pH levels, while at circumneutral to basic pH, REE frequently occur as carbonate and dicarbonate ions (Brookins 1989; Wood 1990; Johannesson *et al.* 1996). In addition, fluoride and phosphate complexes may be important where ligand concentrations are high (Wood 1990; Shand *et al.* 2005). The REE display strong sorption characteristics, particularly at high pH, onto mineral surfaces which reduces REE abundance in solution.

Previous examination of the REE in near neutral to low acidic pH groundwaters (pH 5.4–6.8), indicate that inheritance of rock REE signatures, as a result of solid–liquid exchange reactions such as dissolution/precipitation, cation exchange, weathering reactions, and/or leaching, plays an important role in the origin of the aqueous REE signatures (Smedley 1991; Johannesson *et al.* 2000). Among the assessed bot-

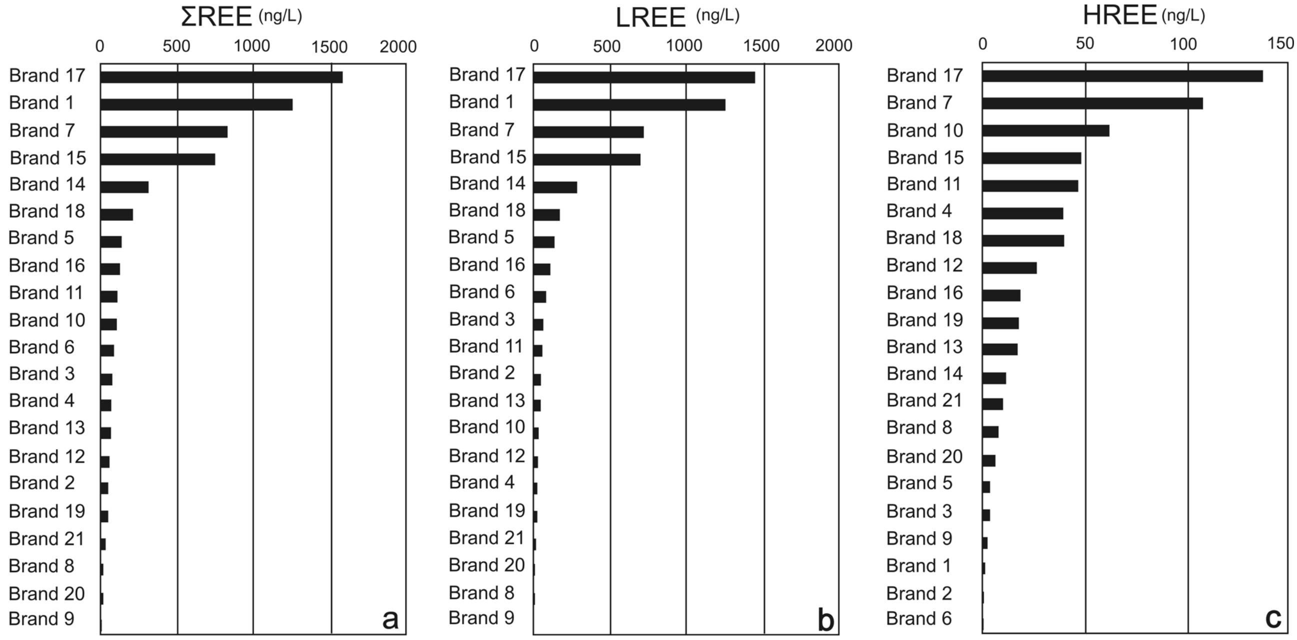

Fig. 4. Total REE (a), LREE (b) and HREE (c) in bottled water samples.

tled water samples, the pH levels in that range characterized naturally carbonated waters, where REE complexation is generally dominated by the formation of carbonate complexes, $LnCO_3^+$ and $Ln(CO_3)_2^-$.

HREE occurrences in the bottled water samples were associated with the formation of carbonate complexes, particularly the dicarbonate ion (i.e., $Ln(CO_3)_2^-$;), whose stability in groundwater increases with increasing atomic number. In relation to LREE, this contributes to greater stability of the HREE in alkaline groundwaters. Where aquifers are devoid of heavy lanthanide–carrying minerals, only light lanthanides are found. If lithological conditions for the occurrence of HREE in groundwater exist, they will dominate the LREE, particularly at high pH levels, because of both the stability of their dicarbonate forms and the removal of LREE from the groundwater as they are generally scavenged through sorption processes much more than the HREE.

A comparison of naturally carbonated and non–carbonated bottled water samples shows that the addition of a CO_2 rich gas phase has a significant effect on weathering processes. The dominant effect is the creation of relatively acidic, aggressive groundwater that will readily attack silicate minerals, Fe–Mn oxyhydroxide phases and, combined with complexing ligands such as F^-, will lead to high total REE concentrations in groundwater (Shand *et al.* 2005).

It should be noted that the bottled water was technologicaly treated in some cases and this may have lead to reduced REE concentrations. For example, CO_2 degassing increases pH and leads to carbonate precipitation. Due to cooling, silica, sulphides, and/or various oxihydroxides flocculate, and many trace elements are sorbed or co–precipitated. Furthermore, change of pressure and temperature during ascent of water induces formation of metastable components and surface coatings, and ion exchange as a function of fluid flow (Möller 2002).

When plotting the abundance of REE towards the atomic number a zigzag curve is obtained. Such abundance curves are difficult to compare, in particular, if individual elements behave anomalously. For that reason, great number of authors suggested to normalise the REE abundance in water by REE abundance in different materials Cl–chondrite (Anders & Grevesse 1989), PAAS (McLennan 1989), source rocks of waters etc. Normalisation does not alter the abundance, it only visualises changes of trends with respect to the normalisation matter and depicts anomalously enriched or depleted elements (Möller 2002).

Various standard shales or the PAAS (Post Archaean average Australian sedimentary rock (McLennan 1989; Rollinson, 1993) are often taken as being representative for the average composition of the earth's upper crust and form the basis for another suite of normalisation plots. Fig. 5 represents PAAS normalized samples of bottled waters with the highest concentrations of REE. REY patterns show a variety of trends, the deviation from a flat trend is termed fractionation with respect to the normalisation material. The fractionation can be the result of a fractional release from host minerals or fractionated incorporation in alteration minerals (Möller 2002). The figure below shows a positive peak of normalized Eu values. Nearly all the samples exhibited a positive Eu anomaly.

The differing geochemical behaviours of cerium and europium often lead to positive or negative Ce or Eu

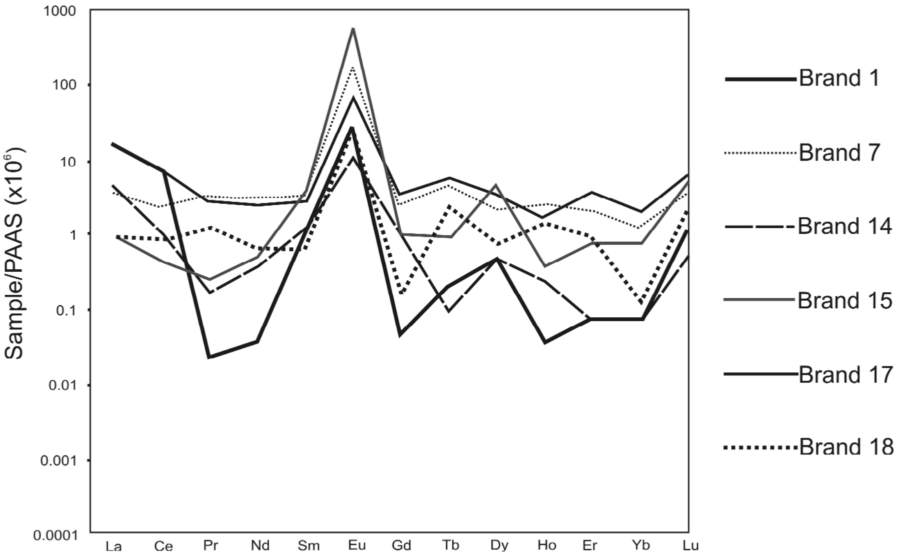

Fig. 5. REE patterns (normalized to PAAS) of bottled water samples.

anomalies in normalised REE distribution plots. Cerium occurs in the Ce^{4+} oxidation state under oxidising conditions and europium is the only lanthanide that, under reducing conditions, can be divalent. The larger size of the divalent Eu ion implies different geochemical substitutions and behaviour from the other REE (BANKS *et al.* 1999). The anomaly is positive if Eu/Eu* or Ce/Ce* > 1, or negative if <1 ($Eu/Eu^*=Eu_N/(Sm_N \times Gd_N)^{0.5}$), ($Ce/Ce^*=Ce_N/(La_N \times Pr_N)^{0.5}$; $_N$ – normalized values) (Fig. 6).

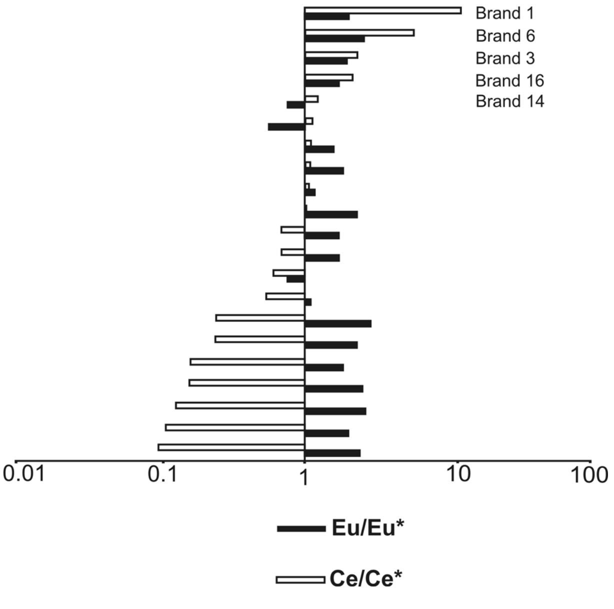

Fig. 6. Ce and Eu anomalies in bottled water samples.

Among the studied samples, a great positive Ce anomaly was noted in four cases. The anomaly is only slightly negative for the high TDS $Na–HCO_3$ water type and especially prominent for the $Ca–Mg–HCO_3$ water type. The negative Ce anomaly may be a result of redox transformations of Ce^{3+} into Ce^{4+}, as anoxic groundwater discharges to the Earth's surface (LEYBOURNE & JOHANNESSON 2008), due to cerianite (CeO_2) precipitation or adsorption to Fe oxyhydroxides (BAU 1999; DIA *et al.* 2000). Experimental data (BAU 1999) indicate that adsorption of Ce onto iron oxydroxides is a relatively slow process so the variations in the magnitude of the Ce anomaly could result in the difference in residence time of circulation groundwater. Negative Ce anomalies are quite common in oxygen rich waters. For instance, seawater, oxygen–rich river and karst waters are characterised world–wide by negative Ce anomalies (MÖLLER 2002).

Contrary to Ce, the positive Eu anomaly was not determined in only three brands. According to the literature, three hypotheses have been proposed for explaining positive Eu anomalies in groundwaters: (i) positive anomalies in the aquifer sediments through which they flow; (ii) preferential dissolution of Eu–enriched minerals (e.g., plagioclase); and (iii) preferential mobilization of Eu^{2+} during water–mineral interaction compared to the trivalent REE (BANKS *et al.* 1999; LEYBOURNE & JOHANNESSON 2008).

Conclusion

Rare earth elements (REE) represent a series of 15 lanthanides (La–Lu) and Y, which exhibits similar geochemical characteristics and has properties comparable to those of heavy lanthanides. The paper presented REE concentrations in samples of 21 bottled water brands. The selection of the bottled water brands was based on different bottling locations, or different geological and hydrogeological conditions that lead to the formation of the chemical compositions of the bottled groundwater. Summary REE concentrations ranged from 5.39 to 1585.82 ng/L. The highest concentrations were recorded in naturally carbonated bottled water samples, as a result of aggressive action of the water (solutional action of CO_2 and low pH levels). Additionally, elevated REE concentrations were found in bottled water samples that reflected specific oxidation–reduction conditions and special lithological compositions of the aquifers. The spatial distribution of HREE in groundwater coincided with granitoid intrusions within Serbia, where

REE–carrying minerals are found. Nearly all the bottled water samples exhibited a positive europium anomaly, indicating specific oxidation–reduction conditions in both the groundwater and the environment in which it circulates.

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Резиме

Елементи ретких земаља у неким флашираним бодама Србије

Елементи ретких земаља (ЕРЗ) анализирани су у 21 узорку флашираних вода са територије Србије. У геохемији термин елементи ретких земаља се генерално посматрано односи на групу елемената који се називају лантаниди (La–Lu) са итријумом. Најпознатија подела лантаниде дели на церијумску групу односно лаке лантаниде (La, Ce, Pr, Nd, Sm, Eu) и итријумску групу односно тешке лантаниде (Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). Итријум (Y) се због сличних геохемијских особина прикључује групи тешких лантанида. ЕРЗ карактерише смањивање јонског радијуса са повећањем атомског броја, што доприноси одређеним разликама у хемијским својствима које су у великој мери предвидиве, а самим тим и корисне у истраживањима ових елемената у различитим срединама. Ниске концентрације ЕРЗ у водама дуго су спречавале њихову примену у истраживањима процеса интеракције вода–стена. Развојем опреме за HR–ICP–MS методу, остварен је значајан помак у истраживању ЕРЗ у водама, како површинским тако и подземним. Овим истраживањима установљен је велики број природних процеса и услова који контролишу понашање ЕРЗ у подземним водама. Утицај литологије на хемијски састав вода је увелико познат, и може довести до значајних разлика у дистрибуцији елемената у подземним водама, и из тог разлога важно је идентификовати хидрогеохемијске процесе који контролишу компоненте у води.

Обрадом параметара преузетих са етикета разматраних флашираних вода, није установљена зависност између појединих макрокомпоненти хемијског састава и ЕРЗ. Исто тако није установљена корелација између укупне минерализације, pH и ЕРЗ. Анализа ЕРЗ у флашираним водама Србије указала је на велики дијапазон концентрација од 5,39 до 1585,82 ng/L. Концентрације лаких лантанида у оквиру разматраних узорака флашираних вода налазе се у границама између 3,62 и 1449,63 ng/L док се тешки лантаниди налазе у значајно мањим концентрацијама од 0 до 136,19 ng/L, што се објашњава чињеницом да лаки лантаниди имају већу распрострањеност у природи. Просторна дистрибуција ЕРЗ у флашираним водама у Србији, условно је потврдила расподелу лантанида према врсти стена; лаки лантаниди се поред киселих, везују и за базичне стене, док тешки лантаниди у водама указују на циркулацију кроз киселе стене (киселе магматске стене и метаморфне и седиментне стене на чије формирање оне имају утицај). Дакле, истовремена појава лаких и тешких лантанида у подземним водама указује на циркулацију у поменутим киселим стенама, док само лаки лантаниди указују на одуство минерала носиоца тешких лантанида у стенама и специфичне оксидо-редукционе услове.

Резултати досадашњих истраживања на територији Србије са аспекта проспекције ЕРЗ, указују да су главни минерали носиоци ЕРЗ монацит, ксенотим, аланит, апатит, бетафит, фергусонит, циркон, колумбит, који су углавном констатовани у гранитоидним стенама и метаморфним стенама непосредног омотача гранита и у наносима потока и река који протичу кроз гранитоидне масиве Цера, Вршца, Букуље, Чемерног, Жељина, Бујановца, Голије итд. Највеће концентрације ЕРЗ и тешких лантанида у флашираним водама се налазе управо у областима ових масива, што се може повезати и са појавом угљен–диоксида у околини Букуље и Бујановца, чија растварачка способност доприноси бржем ослобађању ових елемената из стена. Значајан параметар који утиче на ЕРЗ, посебно лаке лантаниде (La, Ce и Eu) је оксидо–реукциони потенцијал. У већини узорака установљена је негативна аномалија церијума, док скоро сви узорци имају позитивну аномалију еуропијума. Негативна аномалија церијума последица је брзог уклањања Ce из воде и указује на нагле измене оксидо–редукционог потенцијала подземних вода, док позитивна аномалија еуропијума указује на редукциону средину унутар које циркулишу воде, растварање плагиокласа обогаћених Eu или специфичним условима који омогућавају већу миграцију двовалентног еуропијума.

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Distribution of magnesium in groundwater of Serbia

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Abstract. Magnesium is chemical element commonly found in the environment and the main constituent of many types of minerals and rocks. This element is also essential to man. Owing to its abundance in nature, magnesium is present in all water resources and generally occur as the dominant cation, with calcium, in those that feature low TDS levels, whose origin is associated with large formations of sedimentary rocks (limestones, dolomites), and to a lesser extent with the degradation of silicate minerals that contain Mg. Magnesium concentrations in groundwater of Serbia vary over a wide range and their distribution is not uniform, but certain laws of nature do apply. The variation in the concentrations of this ion depends on the considered hydrogeological province, while within a single province it is a consequence of Serbia's highly complex geology. The best examples are the Carpatho-Balkanides, with predominant karstified rock formations, and the Vardar Zone where ophiolites prevail but the makeup is much more complex than that of the Carpatho-Balkanides.

Key words: magnesium, groundwater, distribution, Mg/Ca ratio, Serbia.

Апстракт. Магнезијум је земноалкални метал, веома заступљен у животној средини и главни конституент многих типова минерала и стена, а уједно есенцијалан за човека. Захваљујући великој распрострањености у природи, присутан је у свим водама и обично се са калцијумом, јавља као доминантни катјон у маломинерализованим водама, чије се порекло везује за огромне масе седиментних стена (кречњаци, доломити) и мањим делом за процесе распадања силикатних минерала који садрже магнезијум. Садржај магнезијума у подземним водама Србије варира у веома широком опсегу, дистрибуција је неравномерна, али се могу уочити одређене законoмерности. Варирање концентрација магнезијума у зависности од посматраног рејона, и у оквиру једног рејона је последица веома сложене геолошке грађе Србије. Ово најбоље потврђују примери рејона Карпато-балканида, са доминантним распрострањењем карстификованих стенских маса и рејон Вардарске зоне са доминантним распрострањењем офиолита, али и знатно сложенијом грађом од Карпато-балканида.

Кључне речи: магнезијум, подземне воде, дистрибуција, однос rMg/rCa, Србија.

Introduction

Magnesium is strongly lithophile, the eight most common elemet in the upper lithosphere. Unlike the alkali metals, it is able to built both simple and complex inorganic compounds which are stable under the conditions met in nature (Rankama & Sahama 1950) Magnesium is a significant component of most rock systems and a major constituent of many rock forming minerals (Mittlefehldt 1999; Jović & Jovanović 2004). The chief magnesium-containing minerals are the olivine series, garnets, the pyroxene, amphibolite and mica groups, chrysolite, sepiolite talc, serpentine, the chlorite group, and magnesium-bearing clay minerals. During chemical weathering magnesium is released. Important amounts of magnesium are contained in dolomite and magnesite, and mixtures of these in limestone. Therefore greater geochemical abundance of Mg occur in Mg-rich aquifers, such as olivine-basalts, serpentines, and dolomite rocks; however the absolute magnesium contents in these cases are also low. Minerals with exchange capability adsorb Mg only slightly more firmly than Ca, so that low Mg contents can occasionally be attributed to cation exchange (Davis & DeWiest 1966).

Estimates of Mg concentrations in the lithosphere vary from 132 to 158 mg/g; the highest Mg concentrations tend to be found in ultramafic rocks (Hitchon *et al.*1999). In unpolluted shallow groundwater, magnesium concentrations range from 0.1–1.2 to about 50 mg/L (Cox 1995).

In a sedimentation environment, Mg largely occurs

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in association with the carbonate ion, predominantly as dolomite $CaMg(CO_3)_2$. In the hydrosphere, Mg^{2+} enters by the weathering process, mainly through decomposition of dark ferromagnesian minerals, chlorite, Mg-calcite and dolomite (HITCHON *et al.*1999). Dolomite dissolution and entering Mg in hydrosphere on this way is decribed by reaction (APPELO & POSTMA 1996):

$$CaMg(CO_3)_2 + 2H_2O + 2CO_2 \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3$$

The second important way of groundwater magnesium enrichment is the silicate weathering, particularly of ultramafic rocks made up largely of magnesium silicates, which react rapidly with water (BARNES *et al.* 1978). The most common weathering reaction on earth is the process of hydrolysis, producing new minerals as well as relocation of Mg ions into solution. Minerals which are undergone on this process are relative insoluble, and the final products of this process could be orthosilicic acid and clay minerals. Reactions of pyroxene and biotite decay are shown below (APPELO & POSTMA 1996).

$$\underset{\text{pyroxene}}{[Ca_{1.15}MgAl_{0.3}Si_{1.7}]O_6} + 4.3H^+ + 0.95H_2O \rightarrow$$
$$0.15Al_2Si_2O_5(OH)_3 + 1.15Ca^{2+} + Mg^{2+} + 1.4H_4SiO_4$$

$$\underset{\text{biotite}}{2K[Mg_2Fe][AlSi_3]O_{10}(OH)_2} + 8H^+ + 7H_2O \rightarrow$$
$$Al_2Si_2O_5(OH)_4 + 2K^+ + 4Mg^{2+} + 2Fe(OH)_3 + 4H_4SiO_4$$

$$\underset{\text{olivine}}{5Mg_2SiO_4} + 8H^+ + 2H_2O \rightarrow \underset{\text{serpentine}}{Mg_6(OH)_8Si_4O_{10}} +$$
$$H_4SiO_4 + 4Mg^{2+}$$

Magnesium plays a multiple roles in the human body: it acts directly on the neuromuscular plate, is essential for normal vitamin C and vitamin B_1 activity, takes part in enzymatic processes leading to energy production, reduces coagulation levels, protects the inner walls of blood vessels from fibrosis, and catalyzes the utilization of fats, proteins and carbohydrates (TEOFILOVIĆ *et al.* 1999; TOUYZ & SONTIA 2009; JAHNEN-DECHENT & KETTELER 2012).

Despite the many positive effects and multiple roles in the human body, very large doses of magnesium could have some negative effects. At large oral doses magnesium may cause vomiting and diarrhea, but there are no known cases of magnesium poisoning (MASSRY & SEELIG 1977; SINGH 2010). Too much magnesium does not pose a health risk in healthy individuals because the kidneys eliminate excess amounts in urine (MUSSO 2009). Nevertheless, national drinking water standards have limited the concentration of magnesium in drinking water at 50 mg/L (OFFICIAL GAZETTE OF THE SERBIA AND MONTENEGRO 53/2005).

The geology of Serbia is highly complex and not conducive to generalized studies and assessments. To facilitate insight, hydrogeological provinces have been identified. This hydrogeological zoning is based on geotectonic units, with respect to historical and geological processes, structural-geological conditions, petrological characteristics, geomorphological, physical, geographical, hydrological, hydrometeorological, hydrogeological and other conditions of the environment. In broadly general terms, the provinces are (FILIPOVIĆ *et al.* 2005): the Dacian Basin, the Carpatho-Balkanides, the Serbian Crystalline Core, the Vardar Zone, the Inner Dinarides and the Pannonian Basin (Fig. 1).

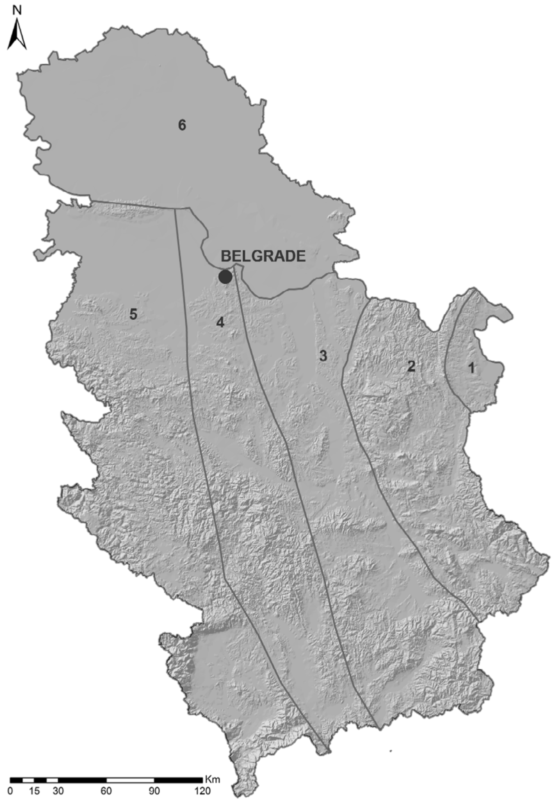

Fig. 1. Hydrogeological provinces of Serbia. Legend: **1,** Dacian Basin; **2,** Carpatho-Balkanides; **3,** Serbian Crystalline Core; **4,** Vardar Zone; **5,** Inner Dinarides; **6,** Pannonian Basin.

The Carpatho-Balkanides are mostly composed of Mesozoic limestones and dolomites which are thick more than 1000 m. Another province, the Serbian Crystalline Core occupies the central part of the territory and it can be divided into two parts. In the north part of Serbian Crystalline Core the most dominant are Neogene and Quaternary sediments in the river valleys, while the south part of Serbian Crystalline Core is composed of very thick Proterozoic metamorphic rocks: gneiss, micaceous shale, various types of schist, marble, quartzite, but also of igneous rocks (intrusive-granitic and volcanic rocks of Tertiary age). The Vardar Zone separates the Serbian Crystalline

Core and the Inner Dinarides. It is characterized by a complex structure consisting of medium grade metamorphosed schist, recrystallized limestones and marbles. In the Inner Dinarides, there is a significant occurrence of Triassic limestones and dolomites, followed by the Jurassic diabase-chert formation (ophiolitic belt) with subordinate limestones in the overlying parts, and the Cretaceous formations with predominatly flysch. The Pannonian Basin, or its south-eastern part in Serbia, consists of Palaeogene, Neogene and Quaternary sediments with a total maximum thickness of about 4000 m (Petrović *et al.* 2012; Filipović *et al.* 2005).

Considering that the Dacian basin has no natural occurrence of groundwater on the surface, but only the presence of highly mineralized chloride-sodium groundwater (brine) with a depth of over 1000, the groundwater occurrences of this zone are not taken into further consideration (Filipović 2003).

Approach and method

The data used in this research were derived from investigations conducted from 2008 to 2012. Groundwater was sampled at 253 locations across Serbia, including groundwater resources featuring low and high total dissolved solids (TDS) levels. The sampling network was designed to evenly cover the entire territory of Serbia and address groundwater occurrences in different rocks (igneous, metamorphic and sedimentary), and consequently different types of aquifers. The sampling points included springs, boreholes and wells. Sampling was conducted in accordance with the Drinking Water Sampling and Laboratory Analysis Rulebook (Official Gazette of the SFRY 33/87). All groundwater samples were tested to determine the main physicochemical parameters (temperature, pH, electrical conductivity) and the basic chemical composition. The analyses were conducted at the Hydrochemistry Lab of the University of Belgrade Faculty of Mining and Geology, as well as at the Public Health Institute of Belgrade. Magnesium concentrations were determined by the ICP-OES method.

Chemical analyses of groundwater samples were statistically processed to assess and interpret hydrochemical data and to generate hydrochemical maps of magnesium distribution in groundwater of Serbia. The data were statistically processed and graphically interpreted using statistical software IBM SPSS v.19. The hydrochemical maps of magnesium distribution in groundwater of Serbia scale 1:500 000 were generated using ESRI ArcGIS 10.0 software.

Results and discussion

General groundwater quality

Serbia's highly complex geology has resulted in groundwater resources featuring different types, temperatures and TDS levels. The dominant anion in the analyzed groundwater samples is the hydrocarbonate ion. Apart from several occurrences of sulfate, chloride, hydrocarbonate-sulfate and hydrocarbonate-chloride types, more than 90 % are found to be of the hydrocarbonate type of groundwater. Of all the analyzed samples, three belong to the sulfate type and two to the chloride group with a chloride share of 97 %equ. The latter two occurrences featured high TDS levels, in excess of 6 g/L. Based on their cation composition, the samples predominantly reflect Ca, Na and composite (Ca-Na, Ca-Mg, Ca-Mg-Na) types of groundwater. Four samples are of the Mg type, with a magnesium share in excess of 75 %equ (Fig. 2).

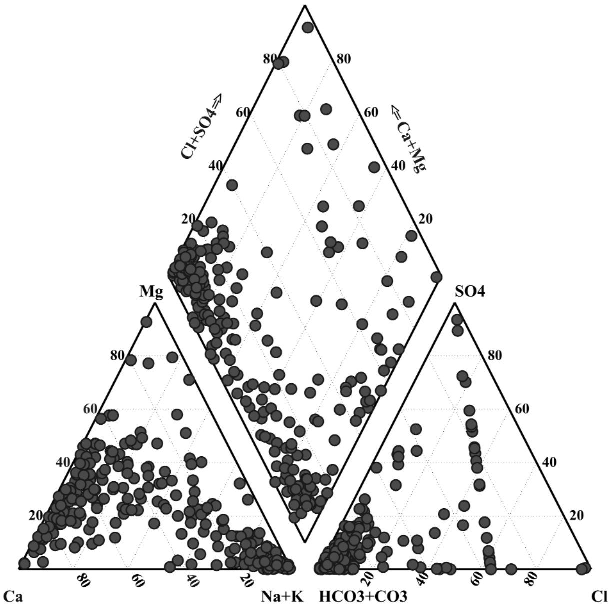

Fig. 2. Piper diagram of the chemical composition of groundwater samples.

With regard to total dissolved solids (TDS), the analyzed samples exhibited considerable diversity: from low levels (only 29 mg/L) to very high levels (in excess of 8 g/L).

Magnesium in groundwater of Serbia

Magnesium concentrations in Serbia's groundwater resources vary considerably, from 0.07 mg/L to 324 mg/L. The average is 32.10 mg/L. Magnesium concentrations in groundwater depend on the geology and tectonics of the ground in which the groundwater is formed, as well as the type of groundwater and the TDS level, given that the concentration of this ion is higher in high-TDS than in low-TDS groundwater, such that this groundwater is not of a pure Mg type.

In most of the samples (121 or 48 %), Mg concentrations are only up to 20 mg/L, while 36 % or 92 samples

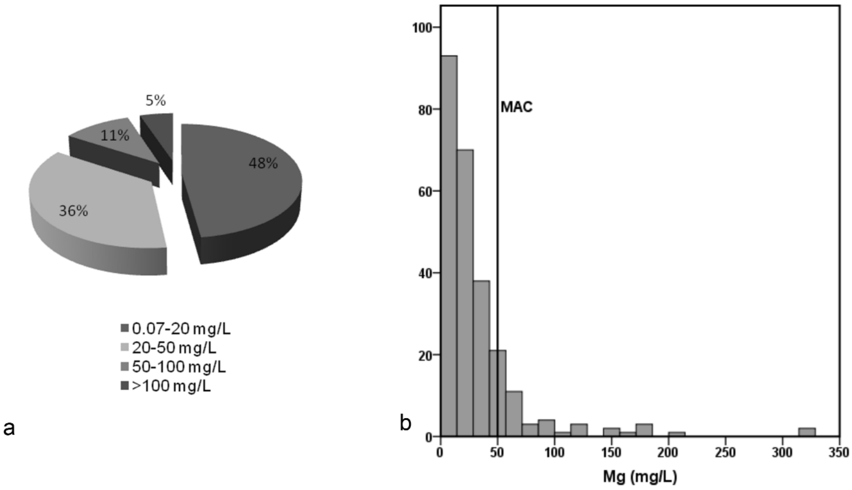

Fig. 3. Plot of relative frequency of Mg (a) and histogram of Mg concentrations in Serbia's groundwater resources (b).

contain 20 to 50 mg/L (Fig. 3a). This means that 84 % of the groundwater samples collected across Serbia exhibited Mg concentrations up to 50 mg/L, which is the maximum allowable concentration (MAC) according to national drinking water standards (OFFICIAL GAZETTE OF THE SERBIA AND MONTENEGRO 53/2005).

As the diagram (Fig. 3b) shows, of the 253 samples, 40 samples (or 16 %) have Mg concentrations in excess of drinking water standards. In view of the total number of samples analyzed and the fact that the MAC for magnesium is considerably lower than for other main cations, such a proportion was expected.

Table 1. Magnesium concentrations in different hydrogeological provinces (mg/L).

Province	Number of samples	min	avr	max
Carpatho-Balkanides (2)	27	0.08	14.40	29.00
Serbian Crystalline Core (3)	26	0.07	40.37	183.00
Vardar Zone (4)	55	0.73	46.33	324.00
Inner Dinarides (5)	67	1.08	22.91	86.00
Pannonian Basin (6)	78	5.60	26.45	65.30

Mg concentrations above 50 mg/L, are found in high-TDS groundwater with TDS more than 1 g/L, where some samples has TDS up to 6 g/L. Such groundwater are generally traced to schists.

In several samples of low-TDS groundwater, Mg concentrations measure 50–60 mg/L; such groundwater is largely genetically associated with rocks like dolomite and dolomitic limestone, as well as interfaces of these rocks with Neogene sediments, flysch, fractured and degraded sandstones and marls, or rocks whose composition includes magnesium-rich minerals. Occurrences of low-TDS groundwater, where Mg concentrations are in the 60–70 mg/L range, were associated with serpentinites, fractured harzburgites and dolomite/serpentinite contacts. This occurenses are usually groundwaters of Mg type.

The distribution of magnesium in groundwater of Serbia is not uniform (Fig. 4.), but regularities resulting from the geological makeup are much more apparent.

Table 1 shows the smallest variations but also the lowest Mg concentrations in the Carpatho-Balkanide Province, where the average Mg concentration is found to be 14.40 mg/L. This province is dominated by limestone and dolomitic karstified rock formations (STEVANOVIĆ 1991) as corroborated by Mg to Ca ratio, hence, maximum Mg concentracion of only 29 mg/L is usual.

The Inner Dinarides of western Serbia exhibited an average Mg concentration in groundwater of 21.91 mg/L; the concentrations of this ion are generally below the MAC, even though there are several exceptions whose concentrations are moderately higher (86 mg/L). The occurrences that give Mg concentrations up to the average level (about 22 mg/L) are generally low-TDS groundwater resources tracing to the limestone formations of this province, with a slight influence of diabase-chert rocks or Neogene sediments. Mg concentrations from the average level to 50 mg/L are recorded in samples collected from groundwater occurrences in limestones under considerable influence from serpentinites, harzburgites and similar rocks that make up the Dinaride ophiolite zone. This province feature a distinct occurrence of groundwater of the Mg type associated with pure serpentinites and harzburgites. This is low-TDS groundwater (350 mg/L), whose Ca concentration is very low Ca (8.02 mg/L) and whose Mg concentration is not too high (66.63 mg/L), though it comprised 92.7 % of the cation composition. The highest concentration of 86 mg/L is recorded in a sample of mineralized groundwater, with TDS of 1260 mg/L, that was formed on the contact between limestons and Neogene sediments (PROTIĆ 1995).

In the Pannonian Basin, Mg concentrations in groundwater are found to range from 5.6 mg/L to 65.30 mg/L. Only one sample with a TDS level of 6095 mg/L has magnesium in concentration above MAC, which is the highest concentration recorded in

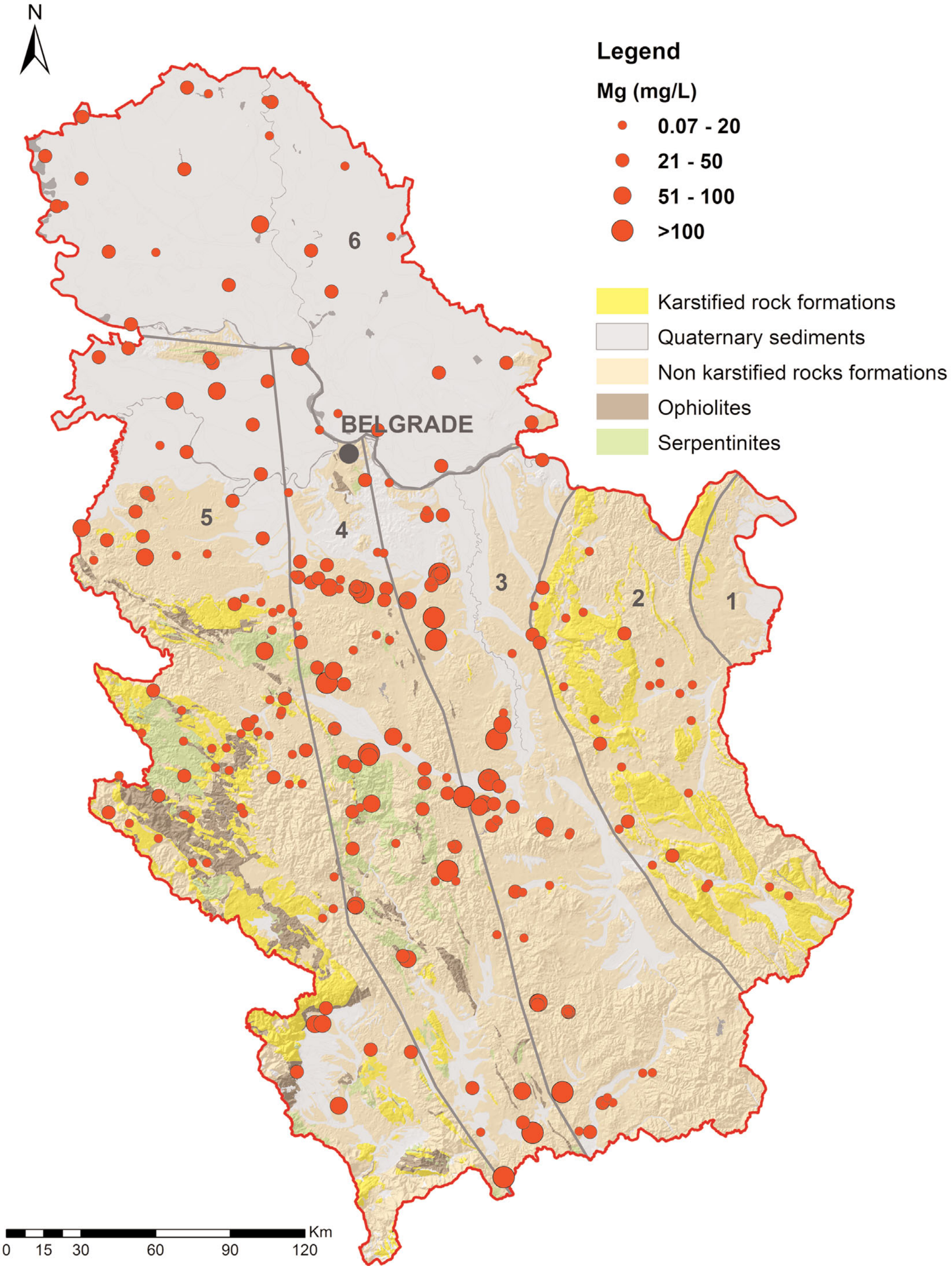

Fig. 4. Distribution of magnesium in Serbia's groundwater resources. Legend: **1,** Dacian Basin; **2,** Carpatho-Balkanides; **3,** Serbian Crystalline Core; **4,** Vardar Zone; **5,** Inner Dinarides; **6,** Pannonian Basin.

the Pannonian Basin (65.30 mg/L). Moderately increased content of Mg on this one groundwater occurrence is a result of the conditions of aquifer forming, at the interface between serpentinites and Tertiary sediments.

Contrary to the previously described provinces, where only a few occurrences of high-TDS groundwater are found to contain high Mg concentrations, the provinces of the Serbian Crystalline Core and Vardar Zone feature the largest number of occurrences with Mg concentrations exceeding 50 mg/L (MAC for drinking water). In the Serbian Crystalline Core, Mg concentrations are found to range from 0.07 mg/L (the lowest recorded in Serbia) to 183 mg/L, with an average concentration of 40.37 mg/L. Fourteen samples give Mg concentrations above 50 mg/L and they could be divided into two groups: (1) groundwater occurrences whose Mg concentrations are from 50 to 70 mg/L and whose composition is under the influence of schists, metasandstones and Neogene sediments containing magnesium-rich silicate minerals, and (2) occurrences of high-TDS groundwater (up to 2777 mg/L) associated with schists, whose Mg concentrations measured from 87 to 183 mg/L.

Mg concentrations in the Vardar Zone groundwater are found to be somewhat higher than in the other four provinces. They are ranged from 0.73 mg/L to 324 mg/L. The average is 46.33 mg/L, which is the highest average Mg concentration among the provinces. Two groups of groundwater occurrences in the Vardar Zone can be identified: (1) groundwater occurrences with Mg concentrations up to MAC (50 mg/L), or around to the average Mg concentration for this province, generally tracing to limestones under the influence of flysch formations, schists and Neogene sediments, and (2) 16 groundwater occurrences whose Mg concentrations are in excess of 50 mg/L, where as many as seven samples have Mg concentrations above 100 mg/L, and two samples in excess of 300 mg/L. Such high Mg concentrations are likely a result of the extent of the ophiolitic belt of the Vardar Zone (Vasković & Matović 2010), as suggested by the rMg/rCa ratio. Vardar Zone ophiolites also influence Mg concentrations of the first group of groundwater occurrences in this province, formed not in ophiolites but other rock formations (primarily karstified Triassic limestones interchanging with less pervious diabase-chert formations and ultramafic rocks).

Mg/Ca ratio in groundwater of Sebia

The Mg/Ca ratio (in mequ) of groundwater is very important because it is an indication of the lithological composition of the aquifer matrix. As such, a Mg/Ca ratio of 0.7 suggests that the groundwater was formed in limestones. Groundwater occurrences with an Mg/Ca ratio of 0.7–0.9 are generally associated with dolomitic limestones, while an Mg/Ca ratio greater than 0.9 is indicative of groundwater tracing to Mg-rich silicate rocks. If the ratio is greater than 1, the groundwater traces to ophiolites and ultramafic rocks, as well as ophiolitic detritus in the sediments (Mandel & Shiftan 1981).

The Mg/Ca ratio of the studied groundwater occurrences in Serbia was found to be from 0.01 to 20.30, suggesting diverse lithological compositions and complex geology, or groundwater occurrences tracing to a variety of rocks. Based on the Mg/Ca ratio, 57 % of the groundwater occurrences traced to limestones, only 11 % to dolomites, and 32 % to silicate rocks, of which 25 % to ophiolites and ultramafic rocks (Fig. 5).

The importance and accuracy of classification of the types of rocks in which groundwater is formed, based on the Mg/Ca ratio, is best demonstrated by the Carpatho-Balkanide Province. There, 30 % of the province features karstified rock formations, in which a karst aquifer was formed (Stevanović 1991). According to the Mg/Ca ratio, 24 of 26 groundwater samples from this province traced to limestones, as corroborated by the geological makeup. One sample exhibit Mg/Ca ratio of 0.87, and their chemical composition was under the influence of dolomites in conjunction with limestones. Also, only one sample has ratio above 0.9, suggesting the presence of silicate rocks and corroborated on the ground by andesites and flysch sediments in a portion of this province, along with dominant Cretaceous limestones. This groundwater occurrence is under the influence of silicate rocks but the aquifer is not formed in them, otherwise it would be much higher.

Looking at the calculated Mg/Ca ratios compared with the geological makeup, it becomes apparent that the Mg/Ca ratio of the rock type in which the groundwater occurs matches the geological makeup, such that this ratio can be used to determine the

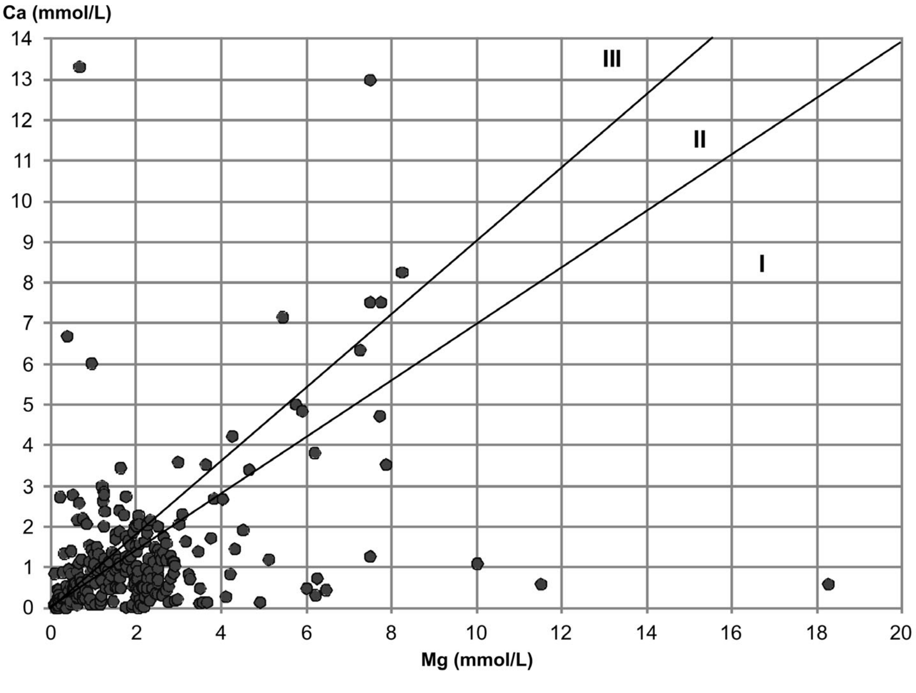

Fig. 5. Magnesium-to-calcium ratio of groundwater. Legend: **I,** Groundwater formed in limestones; **II,** Groundwater associated with dolomites and dolomitic limestones; **III,** Groundwater tracing to magnesium-rich silicate rocks (ophiolites and ultramafic rocks).

genesis of groundwater or at least to narrow down the list of possibilities if data on the geological environment of its origin are not available; in other words, this parameter can be used to determine the effect of lithology on the formation of the chemical composition of groundwater.

Conclusion

It is evident from the results of this research that magnesium concentrations in Serbia's groundwater resources vary over a wide range from 0.07 to 324 mg/L. Uneven distributions and large differences in concentrations have been noted not only between provinces, but also within a single province, as a result of complex geology, attesting to the fact that lithology is the main driver of the chemical composition of groundwater. Additionally, total dissolved solids (TDS) are a very significant parameter as the concentration of this ion, in high-TDS groundwater is considerably higher than in low-TDS groundwater.

Analyses of the Mg/Ca ratio of groundwater in Serbia and the identification of the types of rocks in which groundwater occurs, revealed, based on specified theoretical values, that these ratios largely matched the geological makeup on the ground. It was, therefore, safe to conclude that the Mg/Ca ratio may be used as a parameter for tentative, not definitive, identification of the types of rocks that had a dominant influence on the formation of the chemical composition of groundwater.

The magnesium to calcium ratio is also an important drinking water parameter and the recommended (ideal) ratio of these two ions in water is 1:2. Given that, according to the recommended Mg/Ca ratio more than 60 % of the occurrences of groundwater in Serbia originated in limestones and that quite a few of them exhibit the ideal ratio, such groundwater is precious from a drinking water supply perspective.

Acknowledgements

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Резиме

Дистрибуција магнезијума у подземним водама Србије

Магнезијум је значајан елемент за већину стенских комплекса и битан састојак многих минерала, као што су тамни феромагнезијумски минерали (оливин, пироксени, амфиболи), али и серпентин, талк, бруцит, хлорит, биотит, турмалин, доломит, магнезит, спинел. Садржај Mg у литосфери је различито процењен од 132 до 158 mg/g, а највећи садржаји Mg су у ултрамафитима. У незагађеним, плитким подземним водама садржај магнезијума је од 0,1–1,2 до око 50 mg/L. У процесу распадања стена, Mg^{2+} улази у хидросферу углавном приликом распадања тамних феромагнезијумских минерала, хлорита, магнезијумских калцита и доломита.

У циљу сагледавања начина дистрибуције магнезијума у подземним водама Србије узети су узорци и анализиране су појаве подземних вода (маломинерализованих и минерализованих) са 253 локација у Србији, формиране у различитим стенским масама (магматске, метаморфне, седиментне стене) и које потичу из различитих типова издани. Како је геологија Србије веома сложена, тешко је посматрати и анализирати целокупну територију одједном, па је ради једноставнијег прегледа, анализирање и тумачење података вршено према издвојеним хидрогеолошким рејонима.

На подручју Србије јављају подземне воде различитих типова, температуре као и минерализације, што је последица сложених геолошких услова терена. У анализираним подземним водама минерализација је у опсегу од 29 mg/L до преко 20 g/L. Преовлађујући анјон је HCO_3^-, стога осим неколко појава сулфатних, хлоридних и вода хидрокарбонатно-сулфатног и хидрокарбонатно-хлоридног типа, више од 90 % чине хидрокарбонатне воде. Према катјонском саставу доминирају калцијумске, натријумске или воде мешовитог типа (Ca-Na, Ca-Mg, Ca-Mg-Na). Четири појаве су магнезијумске воде, са уделом магнезијума већим од 75 %екв.

Концентрације магнезијума у подземним водама Србије се крећу у веома широком опсегу од 0,07 до 378 mg/L, док је средњи садржај 32,10 mg/L. Садржај магнезијума у води зависи од гелошке грађе и тектонике терена у којима су формиране воде, типа воде као и минерализације, јер је код минерализованих вода садржај овог јона већи него код маломинерализованих, иако те воде нису по типу чисто магнезијумске. Од укупног броја анализираних појава, концентрације магнезијума код само 18 %, прелазе максималне дозвољене концентрације према правилнику о квалитету воде за пиће (50 mg/L). Појаве код којих су концентрације Mg преко МДК, су генетски углавном везане за стене попут доломита и доломитичних кречњака, као и за контакт ових стена са флишом, неогеним седиментима, испуцалим и распаднутим пешчарима и лапорцима, односно са стенама које у свом саставу садрже магнезијумске минерале. Повишени садржај Mg је детектован и у водама са веома повишеном минерализацијом, најчешће везаним за шкриљце. Концентрације Mg преко 70 mg/L су забележене код вода везаних за серпентините, испуцале харцбургите, контакте доломита и серпентинита.

Дистрибуција магнезијума у подземним водама Србије није равномерна, али се одређене закономерности могу уочити. Неравномерна дистрибуција и велике разлике у концентрацијама могу уочити, не само између различитих рејона, већ и уоквиру једног посматраног рејона, што је последица сложене геолошке грађе терена и доказ да је утицај литологије на формирање хемијског састава подземних вода главни фактор. Поред тога, минерализација воде је веома значајан параметар, јер су концентрације магнезијума у водама високе минерализације значајно веће него у маломинерализованим водама.

Однос rMg/rCa у подземним водама је веома важан јер указује на литолошки састав стена у којима су формиране подземне воде. Однос rMg/rCa у анализираним подземним водама у Србији је у опсегу од 0,01 до 20,30 што указује на разноврсан литолошки састав и сложену геолошку грађу, односно на присуство вода које потичу из различитих стенских маса. На основу односа rMg/rCa, 58 % појава подземних вода потиче из кречњака, само 9 % из доломита, док 33 % појава су воде везане за силикатне стене, од којих 25 % за офиолите и ултрамафите.

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Impact of geo-environmental factors on landslide susceptibility using an AHP method: A case study of Fruška Gora Mt., Serbia

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Abstract. The paper considers the outcome of multi-criteria analysis of landslide susceptibility on the NW outskirts of Fruška Gora Mountain, Serbia. The area of the interest is known for landslide occurrences, and to focus on the most affected areas, it was necessary to consider some principal factors (lithology, slope inclination, rainfall, erosion, vegetation, altitude and slope aspect) and sort them by their importance to the phenomena. Prior to any criteria assessment, available data records had been assembled and refashioned as raster datasets. Thereafter, the criteria arising from an analytical hierarchy process (AHP) provided their weights of preference in the final model. In addition, the model was analysed for the information gain and classified in accordance to the optimal informativeness. Being tailored in the context of raster modelling, aided by the GIS spatial tools, our result gained substantial correlation to the control reference map (a digital photo-geological interpretation map of active and potential landslides).

Key words: GIS, landslide susceptibility, raster model, AHP, photo geological map, Fruška Gora Mt., northern Serbia.

Апстракт. У раду су приказани резултати више-критеријумске анализе склоности ка појави клизипшта на СЗ падинама Фрушке горе. Подручје је иначе познато по појавама клизишта и у циљу да се назначе најугроженија подручја било је неопходно размотрити утицај најзначајнијих фактора који утичу на појаву клизишта (литолошке јединице, нагиб падина, количина падавина, утицај ерозије, утицај вегетације, висина и експозиција падина) и сортирати их н аоснову значаја њиховог утицаја на процес клижења. Пре саме анализе критеријума за сортирање фактора, доступни подаци су прикупљени и припремљени у форми растерских сетова података. Критеријум за сортирање добијен је помоћу Analytical Hierarchy Process (AHP) анализе, која је дала тежинске факторе за сваки од појединих фактора, неопходних за коначни модел. Такође је сам коначни модел додатно испитан са становишта информативности (Information Gain) и класификован у складу са оптималном информативношћу. Коначни модел, који представља растерски модел и који је изведен у ГИС окружењу, дао је добре резултате, који су у корелацији са постојећим катастром клизишта (дигиталном фото-геолошком интерпретацијом на којој су приказана клизишта са активним и привремено умиреним процесом).

Кључне речи: ГИС, склоност ка појави клизишта, растерски модел, AHP, фото-геолошка карта, Фрушка гора, северна Србија.

Introduction

Over the past few decades, the geographic information system (GIS) has been applied to a variety of spatial-related problems. Throughout this period, the applications of its use have been proliferating, achieving more and more impressive results. Thus far, the improvement has affected many fields of science and engineering, but the practice of GIS use has not been equally pervasive around the world (Alleottti & Chowdury 1999, Chacón *et al.* 2006). Namely, sufficiently developed GIS usage in developed countries contrasts with the situation in developing countries, which results in unbalanced insights regarding natural

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phenomena. Engineering geology practice in Serbia is an example of the latter. This paper represents an attempt of the above-mentioned implementation of the GIS within an engineering geology scope.

Environmental hazards, which are addressed within the field of engineering geology, affect both the social and the economic aspects of human lives. Hazards strike at different rates, with varying intervals and duration, leading to different outcomes. Hence, it becomes desirable, if not necessary, to predict their behaviour, number and severity prior to their potential triggering. It has been shown that GIS-based techniques are powerful tools for handling such challenges (Chacón *et al.* 2006; Bonham-Carter 1994).

Herein, one of the most widespread hazard phenomena (Alleottti & Chowdury 1999; Smith 2001), more precisely their susceptibility, is to be considered. This addresses landslides and mass movements alike.

Case study area

The study area is located in the NW part of Serbia, on the mountain Fruška Gora, in the vicinity of Novi Sad. The site is contoured by the river terrace of the Danube on the north, the central mountain's ridge on the south and local ridges along east and west (Fig. 1). The area spreads over approximately 85 km^2 of hilly landscape, with intriguing geoenvironmental features. As such, it has been widely studied in many aspects, including slope stability, and this paper is another contribution in this regard. Prior to any modelling and for the sake of appreciating the phenomena thoroughly, it is advisable to consider all of the environmental factors that are important for slope stability. Thus, only natural factors have been regarded, despite the apparent influence of human activity on slope stability. Hence, considered factors comprise climatic features, lithology and other aspects of geological setting, geomorphological characteristics, hydrological, hydrogeological features and finally, engineering geological properties. A brief presentation of some essential properties follows.

Although it is not of significant altitude (with the summit being slightly over 500 m), this mountain exhibits some climatic variability, particularly in the distribution of rainfall regime and intensity, which varies drastically from the base to the high-ground. This implies that the mountain shape and disposition, rather than its altitude, influence the distribution of moist air masses and the overall precipitation. Namely, moist air abuts the northern slopes and condenses upward, as the temperature decreases (by 1°C/200 m). On the contrary, as it descends down the southern slopes, moist air abuts a warmer environment and accordingly provides less rainfall. This effect is magnified due to the asymmetry of Fruška Gora Mt. because northern slopes rise abruptly in altitude, and mild southern ones gradually subside to a plain. The studied area belongs to the northern, moister realm, with drastic changes in rainfall (gradient of approximately 36 mm/100 m). These changes have a great impact on slope stability and erosion.

The geological setting of the entire Fruška Gora Mt. implies a zonal lithological and structural setting because of the complex horst-anticline forming the core of the mountain. The study area encompasses the NW part of this anticline, with the typical succession (Fig. 5a), starting with low-grade the Paleozoic crystal schists in the anticline base. Scattered in the stripe-like segments, these metamorphic associations occupy the higher ground. They are characterised as a green formation, composed of a mixture of altered magmatic and sedimentary rocks, with regional faults and folds of W–E trends within. Subsequently, a portion of the Triassic basal sediments (conglomerates and sandstones) gradually shifted towards limestone, implying localised subsidence of the paleo-relief at the time. This lasted until the early Jurassic, when another intense uplift occurred, followed by some minor volcanic activity. During the Jurassic period, the far more prominent movement was the one related to the closing of the oceanic basin on the south, which left peridotite (serpentinite) thrusts and diapirs as evidence of this event. This movement culminated in the early Cretaceous, followed by minor gulf formations of coral limestone sequences, known as the Bačko-Banatska zone. The Post-Mesozoic tectonics had re-established W–E trends of structures at regional scale and induced NW–SE oriented faults, traversing the former structures. The tertiary is chiefly represented by marine clastites, gaining more carbonate components as the basin turned more limnic during the late Neogene. This interval is characterised by diverse lithology, ranging from sands and clays to limestones, via marls and other transitional forms. The most significant and the most widespread Quaternary unit is loess. It covers the lower landscape, flattening it towards the

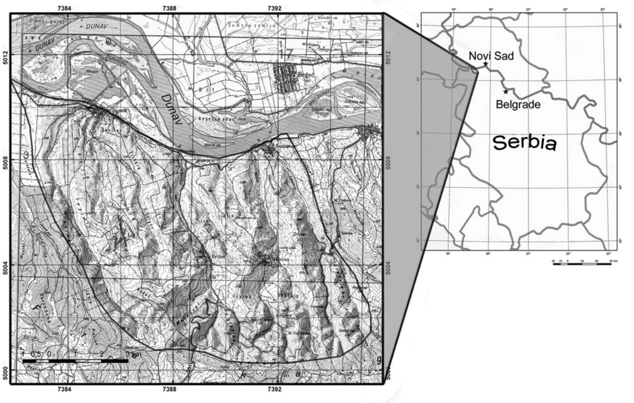

Fig. 1. Geographical location of the study area.

Danube's alluvium and ending with steep cliffs facing the river. The most recent Quaternary unit includes the fluvial deposits of permanent and periodical flows, represented by gravels and sands or their loose aggregations (ČUPKOVIĆ 1997).

Predominant geomorphological entities are of the aeolian and fluvial origin. In conjunction with other processes, these processes sculpted the current landscape of the terrain. Fluvial and aeolian processes alternated in supremacy during the terrain evolution, meaning that they had different enrolments at different times. Apart from these, other morphological processes left some significant imprints, such as larger landslides, proluvial fans and cones, scree slopes and gullies.

Hydrological and hydrogeological regimes are not overlapping the meteorological one, even though such overlapping could be expected. This discrepancy is again influenced by complex geological features. The ultimate aquifers are the Paleozoic schists due to their super-sized voids (i.e., the outcomes of multiple tectonic actions). As such, they provide a more balanced regime (minute annual variations of water table levels) and more constant water temperatures during the year, implying minor direct influence of meteorological phenomena (PETKOVIĆ *et al.* 1976). The water balance analysis suggests that only 30% of the atmospheric precipitation runs out surficially, whereas the rest leaves in evapo-transpiration or as groundwater. Hence, it is more likely that springs and streams are governed by the groundwater regime. Generally, there could be three to four major groundwater horizons specified in the schistosity core, and many smaller localised accumulations in different aquifers. It could be inferred that the former are the most important for the overall water regime of the area, whereas the latter still could be significant by their local influence on the slope stability.

As for the engineering geological properties, it is necessary to stress that surveys have not yet been sufficiently detailed. Seismological features imply relatively stable ground, even though an active fault zone propagates throughout the midst of the mountain, creating possible seismic hazards, especially in loose rock masses. Apparently, the study area seems to be sufficient in size and distance from this zone to be regarded as uniformly affected by minute seismic inconveniences from time to time (PAVLOVIĆ *et al.* 2005)

Material and Methods

Initially, our approach addresses the optimal selection of scale versus complexity of the problem to be modelled. At this point, the chosen mid-scale (1:50000) tolerates not only the extent of approximation or even exclusion of some factors but also certain subjectivity in the selection of class intervals (SÜZEN 2004). The former corresponds to the combination of the heuristic and semi-quantitative approach, which is believed to provide high quality insight in regard to susceptibility, hazard or risk assessment (VAN WESTEN *et al.* 2006). Thus, the landslide susceptibility has been accessed in a somewhat subjective manner, but the inevitable subjectivity adhered to herein appears to be quite desirable.

Modelling was tailored in a sense of multi-criteria analysis, whereas natural environmental factors have been chosen as individual criterions. Refashioned by the scope and the requirements of this research, the modelling procedure generally fits the usual patterns of similar problems (Fig. 2). Initially, it addressed the digital elevation model (DEM), essential for the other implemented models. Additionally, it encompasses the following: rainfall distribution, altitude, aspect and slope models, linear erosion pattern, vegetation distribution and finally, the lithology model.

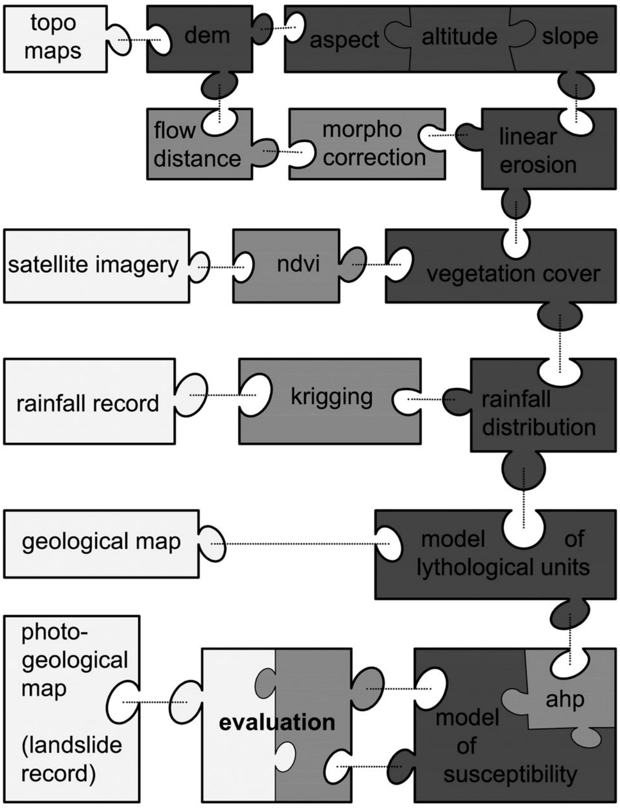

Fig. 2. Schematic display of the research procedure and resources (light grey pieces stand for source data, medium grey for the analyses and calculations, whereas dark-grey ones mark the modelled outcomes).

- DEM was derived from digitised topographic map at 30-m resolution (the same as in all of the following data sets). To increase precision and flatten the outliers such as hill peaks or minor depressions, the DEM was adjusted with tools at hand (standard tools

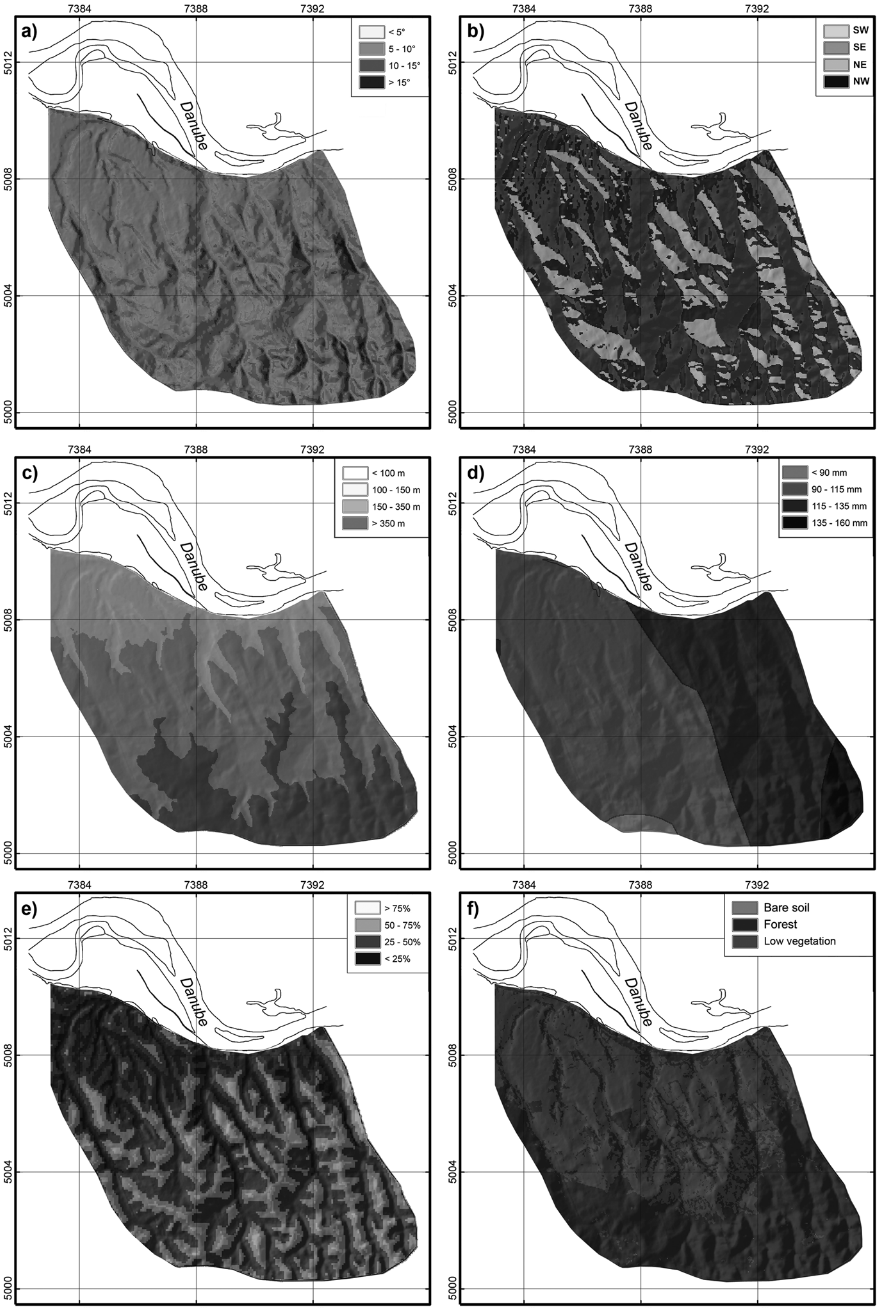

Fig. 3. Raster data sets representing factors of the environment: **a,** slope inclination; **b,** slope aspect; **c,** altitude; **d,** rainfall distribution; **e,** linear erosion; **f,** vegetation cover.

of Watershed analysis, ArcGIS package). Its original digital number (DN), extending from 0 to 255, was reclassified to a range from 0 to 100. Resembling the percentages, reclassified DEM eased the merging with other models, including the models derived from DEM itself.

- The slope inclination model is considered to be of great importance because of its direct physical relation to the slope instability. Moreover, there are empiric proportions on how the inclination relates slope stability in homogeneous masses (GIRAUD 2007). Practically, the slope model is another morphometric feature derived directly from DEM. Because thorough classification would require extensive field work, general assumptions on slope inclination intervals were adopted as imposed by a host of authors (ABOLMASOV 1997; VOŽENÍLEK 2000; GIRAUD 2007,). They suggest distinction between several classes, particularly 0–5°, 5–10°, 10–15° and >15°, where the last two classes include very susceptible slopes, responsible for approximately 95% of landslide occurrences in similar area. All of the classes are assigned DN values according to the proneness they induce. Greater angles make slopes more prone to sliding, and lesser angles make slopes less prone to sliding. It should be stressed that this proportion couples all types of slope instabilities, not only landslides (which, in particular, rarely exceed 15–20°) but also landfalls, creeps, debris flows, etc. Moreover, it is apparent that the critical slope angles entirely depend on geological setting (lithological content and structural features). This is exactly why the criterion has been conferred with references of authors that have addressed this problematic more thoroughly (Fig. 3a).

- Slope aspect is usually a factor with minor influence and tends to be excluded in cases where several other factors contribute in greater proportion. Here it will be considered, but will be given appropriately inferior weight in the final model. Generally, this model substitutes environmental phenomena such as changes in the moisture content or changes in depth of the eluvial crust, both of which are caused by seasonal and diurnal variations of the solar path. At the longitudes in question, it could be expected that northern slopes would retain higher moisture content, whereas southern ones would have more profound eluvium, which leads to a dilemma regarding how to classify this model. Nevertheless, the study area is rich in forestall vegetation, which reduces the crust depth and provides rigidity, but amplifies the moisture absorption. Therefore, the slope stability is primarily influenced by the moisture content as far as the aspect model is concerned (the variation in depth of eluvium could be justifiably excluded from the model). The slope aspect parameter discriminates between these phenomena as follows: NW slopes indicate the most adverse conditions (highest moisture content in the soil) and yield the highest DN values. Conversely, SW slopes provide the most favourable conditions (lower moisture, lower DN values), while moderate conditions characterise NE and SE slopes (Fig. 3b).

- The altitude model follows from the DEM as another morphometric feature. Terrain is classified into four altitude entities (Fig. 3c). Governed by the natural break divisions, a certain DN value has been assigned to each altitude interval. Because it is more likely that lower slopes offer better conditions and seem less susceptible to sliding, they have been assigned lower DN values than the higher ground.
- The rainfall distribution model depicts the data of the Hydrometeorological Survey of Serbia. Furthermore, this model yields abrupt differences while using records of average rainfall per month, particularly in July. This is when the rainfall varies most substantially, both over single month and single day periods. These particular cases have been processed (Fig. 3d) to simulate the most disadvantageous conditions. The matter of classification is quite delicate, considering that the distribution significantly differs from Gaussian. For this instance, a natural break method (Jenks' method) was used to depict rainfall classes (WEBSTER & OLIVER 2001). Four classes have been accepted, and the appropriate DN values were allocated to each class.
- Geomorphological processes implying flowing water as the medium govern the linear erosion pattern, particularly the drainage pattern of fluvial or proluvial origin. Because lateral erosion propels slope instabilities, geomorphological processes are coupled with the occurrences of landslides. The basic principle suggests that the slope segments in the vicinity of the drainage should suffer a greater impact on their stability than remote, higher segments (ridges). The modelling involved the calculation of the pixel distance (Fig. 3e) from the drainage pattern vector, as well as the classification of the later outcome. The initial distance calculation has been corrected to assign respectively lower DNs to higher slope segments and vice versa because lateral erosion dominates in the area below 200 m (Fig. 4).
- Vegetation cover was modelled due to its beneficial contribution to slope stability, especially because the forestall flora dominates the terrain. Some simple approaches and techniques were engaged to display the model of vegetation distribution. For instance, the normalised distribution vegetation index (NDVI) applies well. It required satellite imagery data, particularly the 3rd and 4th channel of the Landsat TM imagery (RAVI 2002). It uses the differences in reflective responses of vegetation versus bare soil or rock (VINSENT 1997). With regard to raster processing, a simple function combines the imagery, creating the vegetation distribution model. Naturally, the presence of vegetation lowers the slope susceptibility to sliding versus bare soil, so DN values had been specified for two classes: with and without significant vegetation cover (Fig. 3f).

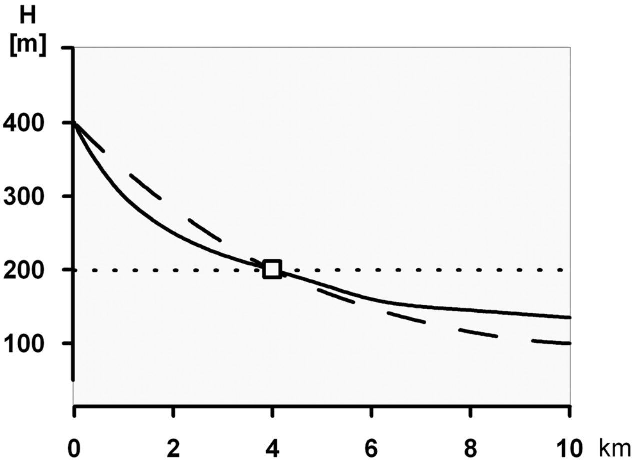

Fig. 4. The cross section of the riverbed (bold line) in comparison to the theoretical curve of erosion basis (dashed line). Note that the interception point borders vertical and lateral erosion preference at approximately 200 m, wherein vertical erosion dominates higher grounds and lateral lower grounds.

- Lithology predominantly determines the susceptibility pattern. However, the geological setting is complex and diverse (Neogene formations especially). To simplify this model, improvised classifications were used, and some different entities were merged into a single class. For example, the common DN value has been allocated to a solid rock masses (Paleozoic) and alluvion (Quaternary) because of their approximately equal unlikeness to host landslides. Accordingly, those are the lowest DN values in this model. In contrast, loose and clayey grounds had the highest DN values (Fig. 5a, b).

Results and Discussion

The final model gathered all of the raster data sets, yielding a susceptibility pattern based on the superposition of their weights (their relative influences). As a convenient procedure that addresses multi-criteria hierarchical structures (GENEST 1994, SAATY 2003, the analytical hierarchy process (AHP) ERCANOGLU *et al.* 2008) has been applied to perform the weighting of the influence for each raster model via a pairwise ratio scale. The foregoing procedure has been fashioned as a visual basic application (VBA) macro for the ArcGIS package (MARINONI 2004).

Prior to obtaining weights, the procedure applied the gross estimation of the factor's preference, based on experts and their experiences (Voženílek 2000; Esmali 2003; Komac 2005; Çađýl *et al.* 2006; Ercanoglu *et al.* 2008). For this instance, a nine-point scale (the range from 1/9 to 9) has been chosen to reflect the pairwise relations between input raster sets, yielding a two-dimensional reciprocal and inconsistent matrix – the comparison matrix (Table 1).

Table 1. AHP comparison matrix.

M$_i$	lithology	slope	rainfall	erosion	vegetation	altitude	aspect
lithology	1,00	1,00	3,00	2,00	4,00	6,00	9,00
slope	1,00	1,00	3,00	2,00	3,00	5,00	8,00
rainfall	0,33	0,33	1,00	2,00	2,00	5,00	4,00
erosion	0,50	0,50	0,50	1,00	3,00	3,00	4,00
vegetation	0,25	0,33	0,50	0,33	1,00	2,00	3,00
altitude	0,17	0,20	0,20	0,33	0,50	1,00	3,00
aspect	0,11	0,13	0,25	0,25	0,33	0,33	1,00
Σ	3,36	3,49	8,45	7,91	13,83	22,33	32,00

Table 2. Final AHP matrix.

M$_i$	lithology	slope	rainfall	erosion	vegetation	altitude	aspect	Sr	%
lithology	0,2976	0,2869	0,3550	0,2528	0,2892	0,2687	0,2902	0,29	29
slope	0,2976	0,2869	0,3550	0,2528	0,2169	0,2239	0,2690	0,27	27
rainfall	0,0982	0,0947	0,1183	0,2528	0,1446	0,2239	0,1511	0,15	15
erosion	0,1488	0,1435	0,0592	0,1264	0,2169	0,1343	0,1363	0,14	14
vegetation	0,0744	0,0947	0,0592	0,0417	0,0723	0,0896	0,0751	0,08	8
altitude	0,0506	0,0574	0,0237	0,0417	0,0362	0,0448	0,0497	0,05	5
aspect	0,0327	0,0359	0,0296	0,0316	0,0239	0,0148	0,0285	0,02	2
λ_{max}=7,33; CI=0,05; RI=1,32								1,00	10

Normalisation of the matrix and averaging by rows generated the priority vector (Saaty 2003, Genest 1994), which represents the distribution of the weights (Table 2, shaded columns). Thereafter, it was necessary to establish the procedure for shifting from an inconsistent to a near-consistent matrix. Versatile solutions proposed by different authors had been considered (Genest 1994, Laininen 2003, Saaty 2003, Po *et al.* 2007). However, they all prove to be slightly different from the outcome of the original technique (Saaty 1977). It was feasible to control the matrix consistency on the simplest basis, i.e., by Saaty's consistency parameters CI and CR (consistency index and consistency ratio, respectively) and criterion (CR<0.1). In this way, the initial subjectivity of the weights distribution (Table 1) has been unbiased up to a certain level, leaving the refined weights depicting the final pattern (Table 2, shaded columns).

Finally, the priority vector or, more appropriately, the linear distribution function of the weights, appeared as follows:

$M = 0.29{\cdot}M_1 + 0.27{\cdot}M_2 + 0.15{\cdot}M_3 + 0.14{\cdot}M_4 + 0.08{\cdot}M_5 + 0.05{\cdot}M_6 + 0.02{\cdot}M_7$

where M_i corresponds to the influence factor's DN values respective to their appearance in the matrices in tables (M_1 = lithology, M_2 = slope,…,M_7 = aspect). As the indices relate to the corresponding factor, the calculus of their weighted DN values generates the final raster – the model of susceptibility (Fig. 5c). This model depicts the spatial distribution of the susceptible zones, separated into four classes: low, mild, moderate and high susceptibility. According to the presented approach, the first class (black in Fig. 5c) corresponds to the areas where the input raster had the smallest contribution, and the fourth class (dark grey in the Fig. 5c) stands for the zone with the highest overall contribution.

In addition, we need to become conversant with the classification criteria used for the final raster. Namely, it has been speculated what number of classes would be optimal for landslide susceptibility maps (Chacón *et al.* 2006). However, there is no decisive formulation on this topic, so we employed the entropy approach (Pászto *et al.* 2009).

We have tested the final raster for the entropy function behaviour over the entire DN span (from 1 to 256 classes) with natural breaks intervals to define the highest information gains (Fig. 6). The trend curve approximates the behaviour of the entropy function,

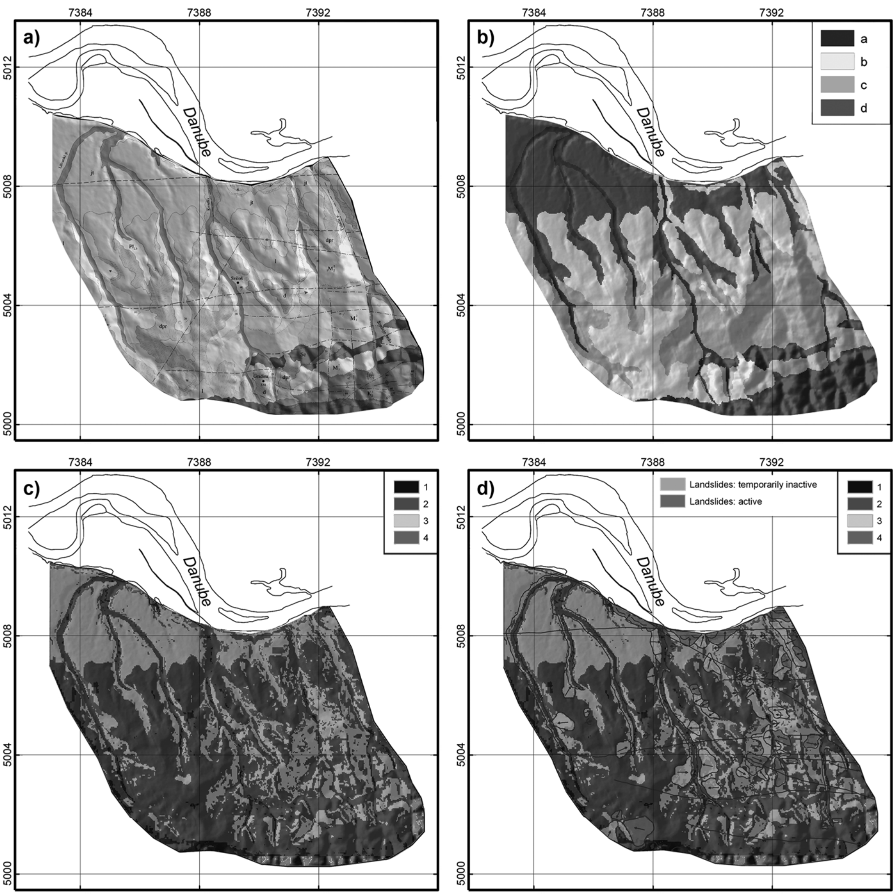

Fig. 5. **a,** Model of lithology (a-alluvion and solid rock, b-loess, c-Tertiary limestone, d-clayey masses and delluvium); **b,** Geological setting (Čupković 1997); **c,** reclassified AHP model of landslide susceptibility (1-low, 2-mild, 3-moderate.

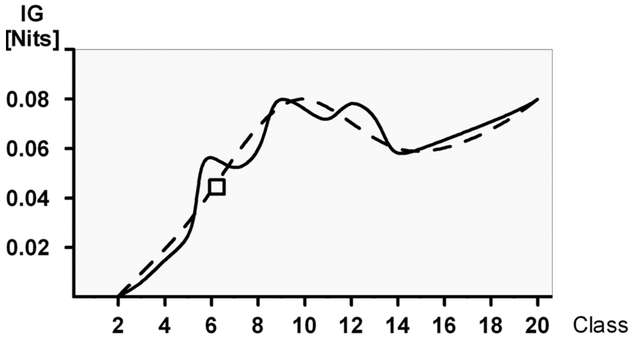

Fig. 6. Information gain of landslide susceptibility model based on the entropy function (the highest gain appears in classes 4 and 9) and four-high susceptibility); d, susceptibility model in comparison to the landslide inventory.

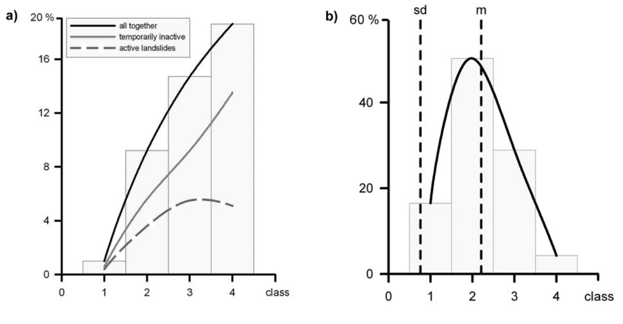

Fig. 7. **a,** histogram of pixel distribution within the landslide polygon area per each susceptibility class (continuous grey line stands for the active landslides, dashed for temporarily inactive ones and the bold black line is overall); **b,** log-normal distribution of data from previous plot with standard deviation, sd, and arithmetic mean, m.

proving the criteria for information analysis. We considered only the span from 2–20 because the trend is fluctuating at higher values. Information gain reaches its maximum when raster is displayed in nine classes, with sub-maximum at four classes, leaving us to choose between these two cases. The former would be quite uncommon in relation to the usual practice, so we have chosen a four-class model (low, mild, moderate, and high susceptibility).

The slope stability map (Pavlović *et al.* 2005) which has been processed through the remote sensing techniques and the fieldwork was used for comparison as a control reference.

The susceptibility map (Fig. 5c) suggests that the area could be qualified as predominantly stable ground, with the second class (mild susceptibility to sliding) widespread. Severely endangered areas are the northern slopes (by the riverbank of the Danube), as well as the internal areas in the NE.

The basic statistical comparison between the model and the landslide inventory (Fig. 5b) resembles the proposed visual evaluation. Figure 7-a reveals that active landslides mostly occupy pixels with values of the fourth class (high susceptibility). The same applies to the category of temporarily inactive landslides; overall, these landslides contain approximately 20% of the fourth class pixels and 14% of the third. However, the terrain, with its portion of the second class exceeding 50% (Fig. 7b), predominantly remains stable but locally inclines to instabilities because by area it is nearly 30% third class (moderate susceptibility).

The numbers of the pixels within the first and the second class are surprising due to the imperfections of the model. Despite these unpredicted inaccuracies, the model yields fairly acceptable predictions of susceptible areas, which precedes possibilities for more detailed assessments, whether concerning susceptibility, hazard or risk.

Conclusion

The final model shows substantial correlation in the most critical areas, as detailed in Fig. 5c. Particularly, the landslide occurrences in valleys in the NE domain parallel the remote sensing data. Every single landslide polygon, either characterised as active or temporarily inactive, encompasses fair quantities of pixel values within the classes of moderate and high susceptibility. Nevertheless, it is obvious that criterions in use were too rigorous in some regions, most likely due to the emphasised influence of the lithology model. In particular, the entire northern outskirts are qualified to be moderately to extremely prone to instabilities, which might not be the case. Priority vector weights have been combined in such a manner to create a dilemma in analysing the results: at some points, our model fits the crucial remote sensing evidence but contradicts it in other regions. Seemingly, this could be avoided by more detailed lithology modelling or filtering the existing model, which would lead to an even more subjective approach, stressing the relevance of heuristics in the analysis.

To improve the final model, further directives must also address the perpetuation of other input data sets. This concerns the DEM, which could be processed in higher resolution, acquiring additional precision for the directly dependable models, such as models of altitude, slope, aspect and even linear erosion pattern. Furthermore, the inputs could be more temporally correlative (this is especially relevant to the rainfall distribution record). Finally, some superior methods in lithological quantification could be used and would minimise the perplexity and subjectivity in the classification. However, the majority of the capitalised adjustments and directives require extensive data, which were unavailable because they demand more detailed surveys.

In essence, the result errs in favour of safety, indicating that large portions of the total area could be potentially triggered. However, this remains arguable and should be regarded cautiously, even though it should not differ from the actual state of susceptibility over the terrain (according to authors such as Komac 2005 or Ercanoglu 2008, where the similar approach matched very rigorous criteria).

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Резиме

Анализа утицаја природних фактора на појаву клизишта помоћу AHP методе - пример на Фрушкој гори

Последњих неколико година сведоци смо повећаног интересовања за феномен клизишта, како у јавном мњењу тако и у научним круговима. Клизишта, у спрези са сродним природним хазардима (поплавама, земљотресима, олујним непогодама итд), свакодневно угрожавају материјална добра и животе људи, нарочито у све гушће насељеним подручјима. Њихово је изучавање са аспекта природног хазарда стога неопходно, како би се последице њиховог дејства, односно ризик од појаве и деловања клизишта правовремено предвидели, спречили или ублажили. Први кораци у процесу анализе хазарда од клизишта, а потом и у коначној процени ризика од истих јесте процена склоности тј. сусцептибилности датог терена ка клижењу. То је уједно и суштина овог рада, који полази од основне претпоставке да се склоност терена ка клижењу може установити на основу сазнања о постојећим примерима појаве клизишта и релевантних података о својствима терена, тј. својствима дате геолошке средине. Притом су усвојена два основна постулата анализе хазарда од клизишта: клижење које се на датом подручју раније догодило може се поновити ако се стекну исти или слични услови који су претходно довели до клижења, а такође се може догодити и на другом подручју сличних својстава, чак и ако није било претходно забележених појава клижења. Склоност појаве клизишта је на тај начин посматрана као просторна вероватноћа појаве и то у тзв. регионалној размери, односно ширем подручју од неколико десетина или стотина километара километарских димензија.

Да би се анализа склоности ка клизиштима успешно извела, тј. да би се та склоност успешно измоделовала неопходно је најпре дефинисати тип клизишта који се узима у разматрање (механизам, врста покретача и резолуција самих појава) а потом прикупити одговарајуће податке. Најпре је потребно прикупити информације о постојећим клизиштима и саставити тзв. катастар клизишта (по могућству у дефинисаном временском интервалу). Затим се прикупљају они подаци који се доводе у директну узрочну везу са појавом клизишта и укључују различите геолошке, геоморфолошке, климатске, хидролошке и хидрогеолошке факторе, као и факторе везане за животну средину. Након тога је могуће направити модел склоности ка клижењу употребом различитих метода, почев од експертских или искуствених, затим једноставних статистичких, детерминистичких и коначно, комплексних статистичко-математичких метода на бази машинског учења. У овом је истраживању конкретно коришћена експертска или искуствена метода *Analytical Hierarchy Process* (*AHP*). Ова метода спада у тзв. више-критеријумске анализе, а користи једноставно спаривање значајних фактора (геолошких, геоморфолошких, климатских, хидролошко-хидрогеолошких и фактора животне средине) на основу квантитативне процене њиховог утицаја на процес клижења (коришћењем предефинисане скале за квантификацију). Процену врше експерти који имају искуства са датим типом клизишта на датом подручју истраживања, независно један од другог, да би се потом њихови критеријуми усагласили. На тај начин се добијају осредњени тежински коефицијенти за сваки од фактора, и њиховим се једноставним сумирањем у ГИС окружењу добија коначан квантитативни модел склоности ка појави клизишта за дати терен на датом подручју. Он се може класификовати у квалитативан модел са назначеним класама, као нпр. класе високе, средње и ниске склоности.

Неопходно је коначно извршити и евалуацију модела, упоређивањем коначног модела са катастром клизишта (упоређивањем просторне дистрибуције клизишта из катастра и рецимо класе високе склоности ка клизању).

Подручје истраживања, површине од око 100 km^2 лоцирано је на СЗ падинама Фрушке горе, уз десну обалу Дунава, између Сусека и Беочина. Присутна су углавном дубока ротациона клизишта у неогеним басенима или у дебелим делувијалним наслагама, дуж падина које су доминантно угрожене дејством линијске ерозије, па се као основни покретач процеса клижења (активирања нових и реактивирања постојећих клизишта) може сматрати линијска ерозија, како мањих токова у залеђу, тако и самог Дунава, који је добро познат по утицају на клизишта дуж своје десне обале. Осим тога, удела има и осцилација подземних вода превасходно изазвана променом режима падавина током године. У геолошком и геоморфолошком смислу, може се рећи да је проучавано подручје предиспонирано за клижење, јер су трошне неогене наслаге, као и дебеле делувијалне наслаге веома распрострањене, а долинске стране релативно стрме (стрмије у односу на јужне падине Фрушке горе) и огољене или евентуално обрасле ниском сезонском вегетацијом (услед пољопривредне активности локалног становништва). Сама клизишта највероватније нису у непосредној вези са геолошким структирама, мада постоје неотектонски активни, чак и сеизмички активни раседи, али су њихове магнитуде занемарљиве када су у питању клизишта. Најзначајнији фактори који утичу на процес су: 1) литолошке јединице, 2) нагиб падина, 3) екстремне падавине, 4) удаљеност од токова са израженом линијском ерозијом, 5) висина, 6) експозиција падина и 7) покривеност вегетацијом. Ови фактори су посредством *AHP* анализе квантификовани тежинским факторима и дали су следећу зависност: $M = 0{,}29 \cdot M_1 + 0{,}27 \cdot M_2 + 0{,}15 \cdot M_3 + 0{,}14 \cdot M_4 + 0{,}08 \cdot M_5 + 0{,}05 \cdot M_6 + 0{,}02 \cdot M_7$, где су индексима од 1–7 респективно означени одговарајући фактори. Добијени модел *M* је потом рекласификован на четири класе склоности: I) ниска, II) блага, III) средња и IV) висока склоност. Расподела класа је дефинисана на основу дистрибуције природних интервала, а број класа је установљен на основу информативности модела, тј. његове ентропије која је тестирана за различит број класа. Преклапањем клизишта из катастра са моделом установљено је да су највише заступљене III и IV класа са 14 % и 20 % од целокупне класе, респективно, док су I и II класа знатно мање заступљене. Упоређивањем коначног модела са контролним катастром клизишта може се дакле установити да су постигнути резултати прихватљиви за квантификацију склоности ка клижењу. Резултати могу бити од велике користи за потребе регионалног планирања, јер пружају квантитативне и квалитативне податке за аспект стабилности терена и делимично, повољност терена за изградњу објеката.

Геолошки анали Балканскога полуострва Annales Géologiques de la Péninsule Balkanique	74	101–102	Београд, децембар 2013 Belgrade, December 2013

In memoriam

Милун Маровић
(1947–2009)

У рано јутро 19. октобра 2009, у саобраћајној несрећи у јужном делу Либије, као члан геолошке експедиције, погинуо је др Милун Маровић, редовни професор Рударско-геолошког факултета Универзитета у Београду.

Професор Милун Маровић рођен је 1947. године у Чачку. Гимназију је завршио у Земуну, а дипломирао је на Рударско-геолошком факултету у Београду 1970. године. Тиме је почела једна богата каријера геолога, истраживача и универзитетског професора. Завршивши магистарске, а потом и докторске студије 1981. године прошао је кроз сва звања, поставши редовни професор са својих 46 година, што је успевало само најбољима. Оваква каријера крунисана је пријемом у Академију инжењерских наука 2004. године.

Цео свој радни век посветио је геологији, а резултати тога рада учинили су га једним од наших најуважаванијих стручњака из тектонике и неотектонике. Научна активност Милуна Маровића била је усмерена на решавање, поред проблема тектонике и неотектонике, већ и сеизмотектонике, структурне геологије, регионалне геологије, као и на развој методике свих ових дисциплина. Проучавао је опште геолошке карактеристике Жагубичког неогеног басена, Букуљског кристаластог комплекса, Лужничког флиша, габро-дијабазног масива код Заовина, креде код Косјерића, појаве туфова код Северова. Свакако један од наших најбољих тектоничара, допринео је познавању тектонског склопа бројних региона, Пријепоља, Полимља, Мокре Горе, Зарожја. Неотектонским истраживањима обухватио је доњи ток Ресаве, Шумадију, северозападну Србију, Алексиначко Поморавље, Колубарско Тамнавски басен, источну Србију, Сокобањски басен, Копаоник, Жељин, Мачву и Поцерину. Резултати истраживања на овим и другим теренима објављени су у преко 120 научних радова штампаних у земљи и иностранству.

Овако богата геолошка каријера обележена је медаљом “Јован Жујовић” коју је добио за допринос развоју регионалне геологије.

Врло предано учествовао је у извођењу наставе. Поред више монографија, аутор је и неколико уџбеника. Преносећи врло успешно резултате савремених истраживања на млађе сараднике стекао је репутацију професора кога су студенти изузетно волели и врло често предлагали за ментора својих радова.

Као што је остварио велики допринос у геологији, тако је био истакнут и у другим пољима. У младости га је занимала музика, имао је свој оркестар, свирао гитару. Кошарком је почео да се бави релативно касно, у својој 21. години. То га, међутим, није спречило да оствари резултате вредне дивљења, и прикупи бројне медаље са олимпијада и светских првенстава. О надасве успешној спортској каријери сведоче Октобарска награда града Београда, Мајска награда Србије, Орден рада са сребрним зрацима и друга признања. Љубав према спорту испољио је и по престанку активног играња, поставши члан представништва Кошаркашког савеза Југославије и Председник Кошаркашког савеза Београда.

Друштвени живот био је у потпуној сагласности са геолошком и спортском каријером. Био је управник Завода за регионалну геологију и палеонтологију, Шеф катедре за динамичку геологију, члан

Међународне асоцијације структурних геолога и тектоничара (International Association of Structural/Tectonic Geologist (IASTG), члан Уређивачког одбора "Геолошких анала Балканскога полуострва", председник државне Комисије за геолошку карту Србије 1:50.000, члан Одбора за природно математичке науке Министарства за науку и технологију Републике Србије, експерт за геологију Савезног министарства за науку и технологију СР Југославије и члан Републичког комитета за образовање.

Све то време био је активан члан Српског геолошког друштва. Међутим геолог таквог формата није себи дозволио само пуко присуство и повремено излагање на зборовима. Поред тога што је у појединим периодима био у Управи Друштва, био је и секретар Савеза геолошких друштава СФРЈ, учествовао је у припреми више геолошких конгреса, а његова каријера је трагично пресечена управо када је изабран за члана научног одбора предстојећег Конгреса геолога Србије.

Милун Маровић је према образовању, дару и таленту, као ретко ко из наше новије авангарде, био човек необичне ерудиције, ентузијазма и изузетне радне енергије, предодређен да оствари успех у било којој области, независно од посла којим се бавио. Рад, воља, и радост су три универзалне категорије, и нека врста принципа и постулата његовог каснијег понашања, а које је он рођењем стекао и које је успешно носио кроз цео свој живот.

Милун је разумео живот у простору и времену. Живео је у садашњости, мада је неком чудном интуицијом и предикцијом умео да предвиди ствари које би се могле догодити и у временима у доласку. Био је надахнут његошевском мудрошћу, веома дубоко поштујући дело овог великана, а што је Милуну давало необичну снагу и лепоту. У том снажном телу биле су саливене врлине и особине које су га красиле, као што су ентузијазам, вера, истрајност, незадовољство достигнутим, научне иновације, креативност, лични шарм, сновиђење, дисперзија пажње, континуираност у раду, и изнад свега честитост, поштење, понос и гордост. Имао је дара и моћ запажања за оно што други нису умели да виде, а сам обично није гледао оно што није могао да сагледа и интерпретира до најмањих детаља. Доласком у нашу средину, Милун је снажно подржавао, а касније и предводио опредељења у којима је увек давана предност остварењу афирмативних, креативних, и стваралачких идеја над крутим стереотипима. Тај стил, дух и став је скоро 40 година био јасно препознатљив и значајан за афирмацију наше групе, смера и катедре. Посебан сегмент личног и заједничког ангажовања, односио се на подизање кадрова, њихову афирмацију и методолошка сазнања које ће им послужити као путоказ, олакшавајући им прелажење пута, као што карта и компас омогућују младом неискусном истраживачу проналажење циља на непознатим и неприступачним теренима.

Као што најчешће бива, после сваког истраживача остају бројни проблеми које је требало решити, бројни послови које је требало завршити... Али остаје и тихо људско сећање. Док траје то сећање, трајаће и наш Милун.

Лука Пешић

Геолошки анали Балканскога полуострва | 74 | 103–104 | Београд, децембар 2013
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In memoriam

Евгений Евгеньевич Милановский
(1923–2012)

Један од одличних изданака руске геолошке школе и науке Е.Е. Милановски преминуо је 11. фебруара 2012. године. Родио се 1. августа 1923. године у Москви. Рођењем, даром и талентом, Е. Евгенијевич је био предодређен да гради универзитетску каријеру. Његов отац Евгениј Владимирович (1892–1940), ученик академика А.П. Павлова, био је професор и шеф Катедре опште геологије на МГРИ.

По окончању другог светског рата и демобилизације, Е. Евгенијевич је обновио започете активности на Катедри историјске геологије Геолошког факултета МГУ, где је дипломирао 1949. године. Теренска проучавања на јужном Уралу обавио је под руководством знаменитог регионалног истраживача и теоретичара геотектонике Н.П. Хераскова. Резултате ових истраживања публиковао је као свој први научни рад 1951. године.

По окончању МГУ, постао је аспирант на катедри, а своја главна истраживања усмерио на неотектонска проучавања и вулканске активности, углавном у Закавказју, Грузији и Јерменији. 1952. године постао је асистент на Катедри за историјску и регионалну геологију по руководством А.А. Богданова, који је 1950. године заменио одлазећег проф. А.Н. Мазаровича. Наставља да ради на факултету, као и у многим експедицијама које су имале регионални научно-истразивачки карактер. Резултати ових обимних истраживања приказани су у успешно одбрањеној кандидатској дисертацији под називом „Геолошка грађа и историја настанка Севанске депресије“ 1953. године. Даље обавља проучавања у централном Казахстану, предложивши нове методе анализе неотектонике Казахстанског горја, које бивају опште прихваћене од стране многих истраживача. У 1955. год. проф. А.А. Богданов је организовао на Геолошком факултету велику тематску Кавкаску експедицију која је у наредних неколико година вршила многобројна комплексна истразивања под руководством знаменитих професора Ажгиреја, Хаина, Славина, Леонова, академика Смирнова и др. Значајну улогу у овим истраживањима имао је, тада већ, доцент Е.Е. Милановски. Поред ових активности шездесетих година прошлог века Е. Евгенијевич, вршио је значајна истраживања у украјинским Карпатима, Динаридима Југославије (у вези са Скопским земљотресом у Македонији 1963.), Балканидима Бугарске и пољским Карпатима, чији су резултати публиковани у неколико монографија.

На основу веома богатог фактографског материјала из тектонике, неотектонике, вулканизма, палеогеографских истраживања и других области регионалне геологије Е. Евгенијевич 1965. године брани са успехом докторску дисертацију пред опонентима Муратовом, Николајевим и Шулцом, а након тога 1967., бива изабран за професора Московског универзитета.

Веома опсежна истраживања Е. Евгенијевич је имао у источној Африци, на Исланду, западној Европи (грабен Осла и Рајнски грабен), на западу Северне Америке, југоисточне Азије у Боливији, где се углавном бави проблемима тектонике, неотектонике, младим вулканским активностима, рифтним системима и средње океанским гребенима. После смрти А.А. Богданова био је (1972) изабран за шефа Катедре за историјску и регионалну геологију МГУ, којом је руководио наредних тридесет година. 1992. изабран је за редовног члана Руске академије наука. Поред овог значајног признања, одличја и награда, био је члан многих учених друштава и академија, укључујући и наше Српско геолошко друштво и чланство у редакционом одбору Геолошких анала Балканскога полуострва.

Е.Е. Милановски је објавио преко 600 научних радова, 20 уџбеника и монографија, а не мањи значај представља руковођење неколико десетина доктораната и кандидата доктора наука како у Русији тако и из иностранства. Приликом своје четврте посете Институту регионалне геологије и палеонтологије РГФ-а, угледни редовни члан Руске академије наука и шеф Катедре историјске и регионалне геологије Геолошког факултета Московског универзитета, у књигу утисака (16. јуна 1995.), записао је: ”С великим дивљењем могу да приметим да геолошка школа Београдског универзитета која има славну и давну традицију и велика достигнућа, продужава да се успешно развија новим младим покољењима српских геолога. Хтео бих да пожелим драгим колегама Геолошког института Београдског универзитета нова значајна достигнућа у геолошким наукама Србије и Балканског полуострва и развој заједничке (другарске) сарадње са геолозима Московског универзитета и целе Русије”. Одласком Е. Евгенијевича руска геолошка школа и наука изгубили су једног изузетног ствараоца и посленика културе (музика, сликарство, књижевност...), чији ће допринос процењивати будуће генерације, а ми српски геолози и аутор ових редова, изгубили смо драгог, оданог и искреног пријатеља и сарадника, који нам је несебично помагао и зато:

Нека је слава и хвала Евгенију Евгенијевичу Милановском.

Лука Пешић

Science and Technology Center Naftagas

Scientific and Technological Centre NIS - Naftagas (STC NIS - Naftagas) is an affiliate company of Serbian Petroleum Industry (*Naftna Industrija Srbije*) (NIS jsc), registered on 10 February 2012 with its headquarters in the city of Novi Sad.

The history of STC of NIS - Naftagas starts in late 2009, when several interrelated business units got together within NIS jsc, with more than 40 years tradition in these regions in research, designing and engineering. The Scientific and Technological Centre has been set up to offer scientific and technical support to NIS jsc core business and provide development and innovation within its business operation.

CORE BUSINESS

Pursuant to the strategy devised by the parent company, NIS jsc, STC NIS - Naftagas main areas of operation are the following: conducting scientific research and development, geological exploration, design and supervision of geophysical works, processing and interpretation of geological and physical data, geological modeling and assessment and calculation of HC reserves, drafting projects related to developing and monitoring of reservoirs, providing engineering services, laboratory and consulting services, putting together and delivery of industrial environment control programmes and eco monitoring.

GEOLOGY

Geology-wise, STC NIS - Naftagas provides services related to geological exploration design, geology interpretation and calculation of (HC) hydrocarbon reserves, drafting projects and designs related to hydro-geology, mining and engineering geology.

ACTIVITY

Geological Explorations

- Collection, processing, analysis и synthesis of geological data
- Expert petrological-sedimentological, micropalaentological, lithostratigraphical, geochemical and petro physical analysis, synthesis and interpretation
- Complex interpretation data geophysical logging
- Complex seismic and geological interpretation
- Drafting of crude and gas exploration programmes
- Drafting regional and detail exploration projects
- Evaluation of tender documentation and assessment of geological risks in concession activity
- Drafting suggestions related to locations and documentation for the conduct of exploration wells and seismic surveys
- Drafting abridged mining projects for drilling and well testing
- Owner's supervision of project delivery

Geological interpretation and HC reserves assessment

- Complex and detailed seismo-geological interpretation
- Drafting reservoirs' structural and petrophysical models
- Geological 3 D modelling и calculation of geological reserves
- Interpretation and synthesis of petrological and sedimentological, petrophysical and palaentological data
- Lithological-stratigraphic interpretation of areas
- Complex interpretation of geophysical logging data
- Identification and characterisation of parent rocks
- Characterisation of crude
- Determination of reservoir genesis
- Assessment of generating potential of exploration area

Hydro-geology, mining and engineering geology

- Drafting design documentation for all type of hydrogeological exploration (tapping into geothermal power, water supply provision, environment protection)
- Design of water abstraction facilities (hydrothermal wells, wells and piezometers) and work performance supervision
- Drafting Study on underground water reserves and results of hydrogeological exploration
- Analysis of hydrogeological conditions of soil and assessment of possibility to abstract underground water with the evaluation of prospects for the needs of thermal energy use, water supply and bottling.

GEOPHYSICS

In the field of geophysics STC Naftagas has been providing geophysical exploration designs, geophysical data processing, and supervision in all phases of geophysical activities, also assessing their quality.

ACTIVITY

- Design of geophysical exploration
- Supervision of the geophysical exploration and quality control
- Geophysical data processing
- AVO/AVA inversion
- Seismic reservoir characterization
- Interpretation and visualization of geophysical data
- Quality rating of geophysical activities
- Testing of underground product lines (cathodic protection checkup)
- Development and implementation of projects for the use of geophysical methods in the field of environmental protection (determining the volume of petroleum/ petroleum product-contaminated soil and groundwater).

RESERVOIR DEVELOPMENT

STC Naftagas provides the designing and monitoring of reservoir development, the analysis and consolidation of specialized data, as well as the complex scientific and technical support to the process of petroleum production, starting from the interpretation of the well test measurements in the process of exploration through reserve “management”, all until reservoir recovery and closing down.

ACTIVITY

Hydrodynamic exploration, analysis and monitoring the reservoir development

Preparation of current and prospective exploration plans for developmental wells and reservoirs

- Data processing and analysis of hydrodynamic measurements and tests
  - Analysis of fluid data
  - Analysis of well testing
  - Analysis of well performance
  - Analysis of reservoir performance
  - PVT analysis
  - Reservoir pressure and temperature
  - Fluid production
  - Water confluence
  - GOR
- Preparation of isobar maps by developmental facilities at specific time intervals
- Processing and interpretation of the measured data in wells (diagnosis, analysis, result)
- Analytical technologies
  - Pressure drop testing in wells
  - Pressure rise testing in wells
  - Interpretation of static and dynamic pressures in wells
  - Interference testing between wells - Pulse Test
  - Well yield test - Limit Test
  - Production Log Test interpretation

Hydrodynamic modeling

- Organization of effective reservoir development, aimed at the rational use of petroleum and gas reserves
- Development of dynamic reservoir model, the design and development monitoring
- Preparation of development projects, calculation of balance and extractable HC reserves
- Elaboration of the petroleum exploitation coefficient
- Calculation of geological, balance and recoverable reserves in the reservoir

Designing and planning perspective reservoir development

- Preparation and analysis of exploitation network of production wells on the reservoir
- Assessment of future production from reservoirs
- Making a schedule of future production from reservoirs
- Participation in the development of petroleum and gas production plans
- Analysis of the development of oil and gas reservoirs
- Development of projects for the introduction of new developmental technologies

Analysis of the situation and the well and reservoir production

- Analysis of production regime
- Analysis of water confluence
- Analysis of GOR
- Movement of water in reservoir
- Movement of gas in reservoir
- Analysis of HC reserves exploitation
- Analysis of the prospects of implementing new GTA

Feasibility study

- Display of exploitation conditions and mode of hydrocarbon preparation
- Preparation of the reservoir production background
- Assessment of hydrocarbons reserves in reservoir
- Proposal for well equipping
- Proposal for the furnishing of collection systems for the preparation of hydrocarbons for transport
- Preparation of production schedule from reservoir
- Calculation of reservoir exploitation characteristics and application on existing systems

CENTRAL LABORATORY

Central Laboratory provides laboratory testing services in the exploration stages, reservoir development, production of petroleum, natural gas, LPG, drinking and thermo-mineral water. Central Laboratory performs environmental monitoring for NIS jsc Novi Sad and third parties (testing of soil, water and air). Laboratory’s relevance has been certified by the accreditation requirements of *ISO/IEC 17025:2006* (109 accredited methods and 8 sampling methods).

Laboratory’s Geological Collection has over 24 thousand meters of cored materials, which, in most cases, give the geological structure of the Pannonian Basin in the territory of Vojvodina.

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Научно-технолошки центар НИС - Нафтагас

Научно-технолошки центар НИС - Нафтагас (НТЦ НИС - Нафтагас) је ћерка компанија Нафтне индустрије Србије (НИС а.д.), регистрована 10. фебруара 2012. године, са седиштем у Новом Саду.

Историја НТЦ НИС - Нафтагас почиње крајем 2009. године спајањем више сродних организационих делова унутар НИС а.д., који на овим просторима имају преко 40 година традиције и искуства у истраживању, пројектовању и инжињерингу. Циљ формирања Научно-техничког центра је пружање научно-техничке подршке основној делатности НИС а.д. и обезбеђење развоја и иновација у оквиру њеног пословања.

ОСНОВНА ДЕЛАТНОСТ

У складу са стратегијом матичне компаније, НИС а.д., основни правци делатности НТЦ НИС - Нафтагас су: извођење научно-истраживачких и развојних радова, пројектовање геолошких истраживања, пројектовање и надзор геофизичких радова, обрада и интерпретација геолошко - геофизичких података, геолошко моделирање и прорачун резерви УВ, израда пројеката разраде, мониторинга лежишта, пружање инжењеринг услуга, лабораторијских и консултантских услуга, израда и реализација програма производне еколошке контроле и еколошког мониторинга.

ГЕОЛОГИЈА

У области геологије НТЦ НИС - Нафтагас пружа услуге пројектовања геолошких истраживања, геолошке интерпретације и прорачуна резерви угљоводоника (УВ), израде пројеката и елабората у хидрогеологији, рудној и инжењерској геологији.

ДЕЛАТНОСТ

Геолошка истраживања

- Прикупљање, обрада, анализа и синтеза геолошких података
- Специјалистичке петролошко-седиментолошке, микропалеонтолошке, литостратиграфске, геохемијске и петрофизичке анализе, синтезе и интерпретације
- Комплексна интерпретација података геофизичког каротажа
- Комплексна сеизмогеолошка интерпретација
- Разрада програма истраживања нафте и гаса
- Израда регионалних и детаљних пројеката истраживања
- Анализа тендерске документације и процена геолошких ризика у концесионој делатности
- Израда предлога локација и документације за извођење истражних бушотина и сеизмичких испитивања
- Израда упрошћених рударских пројеката за бушење и испитивање бушотина
- Ауторски надзор над реализацијом пројеката

Геолошка интерпретација и прорачун резерви УВ

- Комплексна и детаљна сеизмогеолошка интерпретација
- Израда структурног и петрофизичког модела лежишта
- Геолошко 3Д моделирање и прорачун геолошких резерви
- Интерпретација и синтеза петролошко-седиментолошких, петрофизичких и палеонтолошких података
- Литолошко-стратиграфска интерпретација простора
- Комплексна интерпретација података геофизичког каротажа
- Идентификација и карактеризација матичних стена
- Карактеризација нафте
- Дефинисање генезе лежишта
- Процена генеративног потенцијала истражног простора

Хидрогеологија, рудна и инжењерска геологија

- Израда пројектне документације за све врсте хидрогеолошких истраживања (коришћење геотермалне енергије, обезбеђење водоснабдевања, заштита животне средине)
- Пројектовање водозахватних објеката (хидротермалне бушотине, бунари и пијезометри) и надзор над извођењем радова
- Израда Елабората о резервама подземних вода и резултатима хидрогеолошких истраживања
- Анализа хидрогеолошких услова терена и процена могућности захватања подземних вода са оценом перспективности за потребе коришћења топлотне енергије, водоснабдевања и флаширања

ГЕОФИЗИКА

У области геофизике НТЦ НИС - Нафтагас пружа услуге пројектовања геофизичких истраживања, обраде геофизичких података, врши надзор у свим фазама извођења геофизичких радова и оцењује њихов квалитет.

ДЕЛАТНОСТ

- Пројектовање геофизичких истраживања
- Надзор над извођењем геофизичких истраживања и контрола квалитета
- Обрада геофизичких података
- AVO/AVA инверзија
- Сеизмичка карактеризација резервоара
- Интерпретација и визуализација геофизичких података
- Оцена квалитета геофизичких радова
- Испитивање стања подземних продуктовода (провера катодне заштите)
- Израда и реализација пројеката за коришћење геофизичких метода у области заштите животне средине (одређивање обима контаминације земљишта и подземних вода нафтом и нафтним дериватима).

РАЗРАДА ЛЕЖИШТА

НТЦ НИС - Нафтагас пружа услуге пројектовања и мониторинга разраде лежишта, анализе и консолидације специјализованих података, обезбеђује комплексну научно-техничку подршку процесу производње нафте, почев од интерпретације пробних мерења бушотина у процесу истраживања преко „управљања“ резервама, до санације и затварања лежишта.

ДЕЛАТНОСТ

Хидродинамичка истраживања, анализа и мониторинг разраде лежишта

Израда текућих и перспективних планова истраживања разрадних бушотина и планова разраде лежишта

- Обрада и анализа података хидродинамичких мерења и испитивања
    - Анализа података флуида
    - Анализа испитивања бушотина
    - Анализа рада бушотина
    - Анализа рада лежишта
    - PVT анализа
    - Притисак и температура лежишта
    - Производња флуида
    - Уток воде
    - GOR
- Израда карата изобара по објектима разраде у одређеним временским интервалима
- Обрада и интерпретација измерених података у бушотинама (дијагностика, анализа, резултат)
- Аналитичке технологије
    - Испитивање пада притиска у бушотинама
    - Испитивање пораста притиска у бушотинама
    - Интерпретација статичких и динамичких притисака у бушотинама
    - Испитивање интерференције међу бушотинама – Пулс тест
    - Испитивање издашности бушотина - Лимит тест
    - Интерпретација Production log испитивања

Хидродинамичко моделирање

- Организација ефикасне разраде лежишта, усмерене на рационално коришћење резерви нафте и гаса
- Израда динамичког модела лежишта, пројектовање и мониторинг разраде
- Израда пројеката разраде, прорачун билансних и придобивих резерви УВ
- Образлагање коефицијента искоришћења нафте
- Прорачун геолошких, билансних и придобивих резерви у лежишту

Пројектовање и перспективно планирање разраде лежишта

- Израда и анализа експлоатационе мреже производних бушотина на лежишту
- Процена будуће производње из лежишта
- Израда динамике будуће производње из лежишта
- Учешће у изради планова производње нафте и гаса
- Анализа разраде нафтних и гасних лежишта
- Израда пројеката за увођење нових технологија разраде

Анализа стања и производих бушотина и лежишта

- Анализа производног режима
- Анализа утока воде
- Анализа GOR
- Кретање воде у лежишту
- Кретање гаса у лежишту
- Анализа искоришћења резерви УВ
- Анализа перспектива имплементације нових ГТА

Израда студија изводљивости

- Приказ услова и начин експлоатације и припреме угљоводоника
- Израда историјата производње из лежишта
- Оцена резерви угљоводоника у лежишту
- Предлог опремања бушотина
- Предлог опремања сабирних система за припрему угљоводоника за транспорт
- Израда динамике производње из лежишта
- Прорачун експлоатационих карактеристика лежишта и примена на постојећим системима

ЦЕНТРАЛНА ЛАБОРАТОРИЈА

Централна Лабораторија пружа услуге лабораторијских испитивања у фазама истраживања, разраде лежишта, производње нафте, природног гаса, ТНГ, пијаћих и термо-минералних вода.

Централна Лабораторија врши еколошки мониторинг за потребе НИС а.д. Нови Сад и трећих лица (испитивања земљишта, воде и ваздуха). Компетентност Лабораторије је потврђена акредитацијом по захтевима стандарда *SRPS ISO/IEC 17025:2006* (109 акредитованих метода и 8 метода узорковања).

Геолошка збирка Лабораторије броји преко 24 хиљаде метара језгрованог материјала, који, у највећем броју, дају геолошку грађу Панонског басена на територији Војводине.

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Instructions for authors

Geološki anali Balkanskoga poluostrva is issued annally and publishes original scientific contributions over a wide range of topics in any field of the geological sciences. The journal accepts papers in English of moderate length, not exceeding 50 double spaced manuscript pages, including illustrations.

Submit three copies of a double-spaced manuscript and illustrations (good photocopies), plus an electronic version of the manuscript. Leave adequate margins of 3 cm, on all sides, and the right margin unjustified with no automatic hyphenation. Typewritten manuscripts will not be accepted. Do not send large files (e.g. photographic illustrations) as e-mail attachments, but submit them on a CD-ROM sent by air-mail.

Material being described must be registered as part of a formal collection housed in some recognised Institution so that it is accessible and available for study by other workers.

Paper should be arranged as follows: title, name and surname (in full) of author or authors, abstract, key words, adresses (foot note on the 1st page) with a mention of the parent organisation and e-mail address, text, acknowledgements, references, summary, figures, tables, and plate captions.

The title of the paper should be short, but expressing the principal aim of the paper.

The abstract must be concise, not more than 200–250 words, and should be informative, stating the results presented in the article rather than describing its contents. Inclusion of references in the abstract is not recommended.

After the abstract, list 5–8 **keywords** which describe the subject matter of the work. They should be arranged from general to more specific ones.

The text should be written as clear and understandable as possible. Use up to threee levels of headings. Their hierarchy should be indicated in the left-hand margin of the text. Italics are used only for the name of genera and species, or if a word is italicized in the original title. References should be cited in the text as follows: DAMBORANEA (2002) or (DANBORANEA 2002) for a single author; FÜRSICH & HEINZE (1998) or (FÜRSICH & HEINZE 1998), for two authors; RICCARDI *et al.* (1991) or (RICCARDI *et al.* 1991) for multiple-author works.

References should be classified alphabetically according to the author's names. Include only published papers mentioned in the text, unpublished reports will be accepted only in exeptional cases. Do not abbreviate the titles of journals and give the names of symposium volumes and edited books. For books it is necessary to give the publisher's name and place of publication. References in Cyrillic alphabet must be transliterated to the Latin alphabet. The titles of the paper in a non-Latin alphabet should be translated into English with an indication of the original language in parenthases, while the name of the journal must be transliterated into Latin alphabet. Examples are as follows:

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. *Paleontologičeskii Žurnal*, 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.

Illustrations can be submitted as conventional hardcopies or in electronic form. The preferred formats for graphics is CDR (600 dpi) and for photographs and plates TIFF (600 dpi). All original drawings and photographs should be in the form of glossy prints of profesional quality. The illustrations should have a width of 8.4, 12 or 17.5 cm, the final limit is the size of type area (17.5 × 24.5). Lines and letters must be suitable for reduction. It is also recommended to send copies reduced to the size for publication; after reduction, the smallest lettering should be not less then 1 mm and not greater than 4 mm in height (in the Arial font). The aproxiamte position of figures and tables should be indicated in the manuscript margin. Do not incorporate illustrations in the text of the paper. Figure, table and plate captions should be listed on separate sheets. The author's name and figure number should be indicated at the foot of the illustration. The figure numbers can be writen by hand on a paper copy of the plate or on a transparent overlay, not on the plate itself. The cost of printing colour figures must be paid in full by the author.

Authors will receive one and if necessary two **proofs**. These must be returned within the time limit indicated. If this does not happen, the publication of the paper will be postponed automatically to a later date.

25 **reprints** per article will be provided free of charge for the author (in the case of multi-authored papers, the senior author will receive the reprints).

All **correspondence**, enquires and manuscript submissions should be directed to the Editor-in-Chief of *Geološki anali Balkanskoga poluostrva*.

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ГЕОЛОШКИ АНАЛИ БАЛКАНСКОГА ПОЛУОСТРВА
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