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The impact of geology on the migration of fluorides in mineral waters of the Bukulja and Brajkovac pluton area, Serbia

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Abstract. One of the hydrogeochemical parameters that classify groundwater as mineral water is the content of fluoride ions. Their concentration is both important and limited for bottled mineral waters. Hydrochemical research of mineral waters in the surrounding area of Bukulja and Brajkovac pluton, in central Serbia, was conducted in order to define the chemical composition and genesis of these waters. They are carbonated waters, with content of fluoride ranging from 0.2 up to 6.6 mg/L. Since hydrochemical analyses showed variations in the major water chemistry, it was obvious that, apart from hydrochemical research, some explorations of the structure of the regional terrain would be inevitable. For these purposes, some additional geological research was performed, creating an adequate basis for the interpretation of the genesis of these carbonated mineral waters. The results confirmed the significance of the application of hydrochemical methods in the research of mineral waters. The work tended to emphasize that "technological treatment" for decreasing the concentration of fluoride in mineral waters occurs in nature, indicating the existence of natural defluoridization.

Key words: fluorides, hydrogeochemistry, mineral waters, Bukulja and Brajkovac granitoid pluton, defluoridization.

Апстракт. Један од хидрогеохемијских параметара за издвајање подземне воде као минералне је и садржај флуоридног јона. Садржај овог јона је изузетно важан и ограничавајући код флашираних минералних вода. Хидрохемијска истраживања минералних вода у околини плутона Букуље и Брајковца, у централној Србији, су спроведена ради дефинисања хемијског састава и одређивања порекла испитиваних вода. Оне су угљокиселе, са садржајем флуоридног јона од 0,2 до 6,6 mg/l. Пошто су хидрохемијске анализе показале разлику у хемијском саставу макро компоненти, било је јасно да је неопходно спровести и истраживања регионалне грађе. За ове потребе, нека додатна геолошка истраживања су спроведена, стварајући неопходну основу за интерпретацију порекла испитиваних угљокиселих минералних вода. Резултати су потврдили велики значај примене хидрохемијских метода у истраживању минералних вода. „Технолошки третмани" смањења концентрација флуоридног јона у минералним водама се одвијају и у природним условима, указујући на природну дефлуоридизацију.

Кључне речи: флуориди, хидрогеохемија, минералне воде, гранитоидни плутон Букуље и Брајковца, дефлуоридизација.

Introduction

Research of mineral waters is of great importance due to the wide variety of their utilization and consumption. Some of them are used for balneotherapeutic purposes, others as medicinal waters, or in the form of bottled mineral water. It is significant to know the content of trace elements. Set of norms and regulations on natural mineral waters define the minimum as well as the maximum allowed values of the content. Fluoride ions have an important place among trace elements; low values cause dental caries, while high values produce dental fluorosis or even skeletal fluorosis. The optimal values are between 0.5 and 1.5 mg/L (Fordyce

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2011). The impact of fluorides on the physiological functions of the human body is manifold. Fluorides affect normal endocrine function, as well as the function of the central nervous system and the immune system (Committee on Fluoride in Drinking Water, US National Research Council 2006). The overall assumption is that the fluoride content in some mineral waters is important because of hyperactivity the ion in the biological balance of elements in the human body. As was already mentioned, the emphasis is put on the content of fluoride ions in waters which can be used as bottled mineral waters. In this case, hydrogeochemical methods play an important role within hydrogeological investigations. Namely, defining hydrogeological conditions favorable for migrations of these ions aids greatly in the recognition the hydrogeological conditions required for the formation of mineral waters with the optimal content of fluoride. Lithology is definitely regarded as one of key factors for defining the presence of a certain element. This kind of approach allows for the recognition of the main issues of hydrochemistry and hydrogeology, for example mineral water genesis, to establish the conditions and forms of migration of fluoride in groundwater, *etc*. Based on previous investigations, the basic principles have been defined in reference to the migrations of this important trace element in the mineral waters of Serbia (PAPIĆ 1994), and in later hydrochemical investigations, attention was paid to the interdependence of lithology and the presence of fluoride in mineral water. Different fluoride containing minerals are the main sources of fluorides in soil and groundwater (TIRUMALESH 2006; SHAJI 2007) and there is a strong correlation between the lithology of aquifers and the fluoride concentration in groundwater (SEELIG 2010). Relevant fluoride minerals are: amphibole, mica, fluorite (CaF_2), apatite ($Ca_5(PO_4)_3(F,OH,Cl)$), topaz ($Al_2SiO_4(F,OH)_2$) and cryolite (Na_3AlF_6). Granite and pegmatite are especially rich in fluoride minerals (BAILEY 1977; HITCHON 1999; REDDY 2010) and RANKAMA & SAHAMA (1950) mention that rocks rich in alkali metals and volcanic glass contain more fluoride than other magmatic rocks. The fluoride concentration in groundwater is controlled by many geochemical factors. Elevated concentrations of fluoride are associated with high *TDS* values (Total Dissolved Solids), high Na^+ and low Ca^{2+} contents, ion exchange processes, *etc*. (RAFIQUE 2009). High fluoride concentrations occur in groundwaters with low concentrations of calcium, therefore the cation exchange processes, resulting in Ca^{2+} removal from water, provides favorable conditions for fluoride enrichment of groundwaters (FURI 2011). The positive correlation between fluoride content in groundwaters and pH is explained by the fact that the ionic radius of OH^- is nearly identical with that of F^-, allowing them to undergo exchange processes in the crystal structure of minerals. Clay minerals, *e.g.*, kaolinite, have the ability to bind F^- ions on its surface, but if the pH increases, OH^- ions tend to replace F^- ions, whereby F^- ions are consequently released into the groundwater (SREEDEVI 2006). Relatively high fluoride concentrations also occur in groundwater that circulates deep down fault structures (KIM 2005). All of this makes it easier to locate new high-quality groundwater aquifers that satisfy the current requirements and regulations on bottled mineral waters.

Methods

Samples of mineral waters were collected during the investigation period in 2010–2011. Water samples were taken from eight representative localities in the area of Bukulja and Brajkovac granitoid pluton and 16 physico-chemical parameters were determined in these samples, following standard and official methods of analysis. The groundwater samples were filtered through 0.4 μm membrane on site. Unstable hydrochemical parameters were measured on site, immediately after collection of the sample by potentiometry (pH-meter, WTW) and conductometry (EC, WTW). The major anions and fluoride were measured by ion chromatography (IC Dionex ICS 3000 DC). The major cations were determined by inductively coupled plasma – optical emission spectroscopy (ICP–OES, Varian).

The Schlumberger water quality analysis software AquaChem and USGS software Phreeqc were used for processing the hydrogeochemical data. The packages were used for the determination of the mineral saturation indexes and for the construction of charts.

Results

In the following text, eight characteristic localities of mineral waters, with different fluoride contents, are described. They are located in the area of Bukulja Mountain and Brajkovac Village in central Serbia, 60 km south of Belgrade (Fig. 1).

Geology

The region of Bukulja is dominated by a horst structure, which is in the form of an elongated block that stretches ESE–WNW and can be clearly discerned. It is composed of Paleozoic psamite-pelite sediments, which due to regional and contact metamorphism, first transformed into sericite schists and phyllite, and then into micaschists and finally into sericite schists and gneisses which form a contact aureole of Tertiary pluton bodies. The immediate cover of the Bukulja crystalline rock is composed of Cretaceous basal clastic limestones and flysch sediments, which in the course of intrusion of the Bukulja granite monzonite and the Brajkovac granodiorite, underwent some contact metamorphic changes. These are

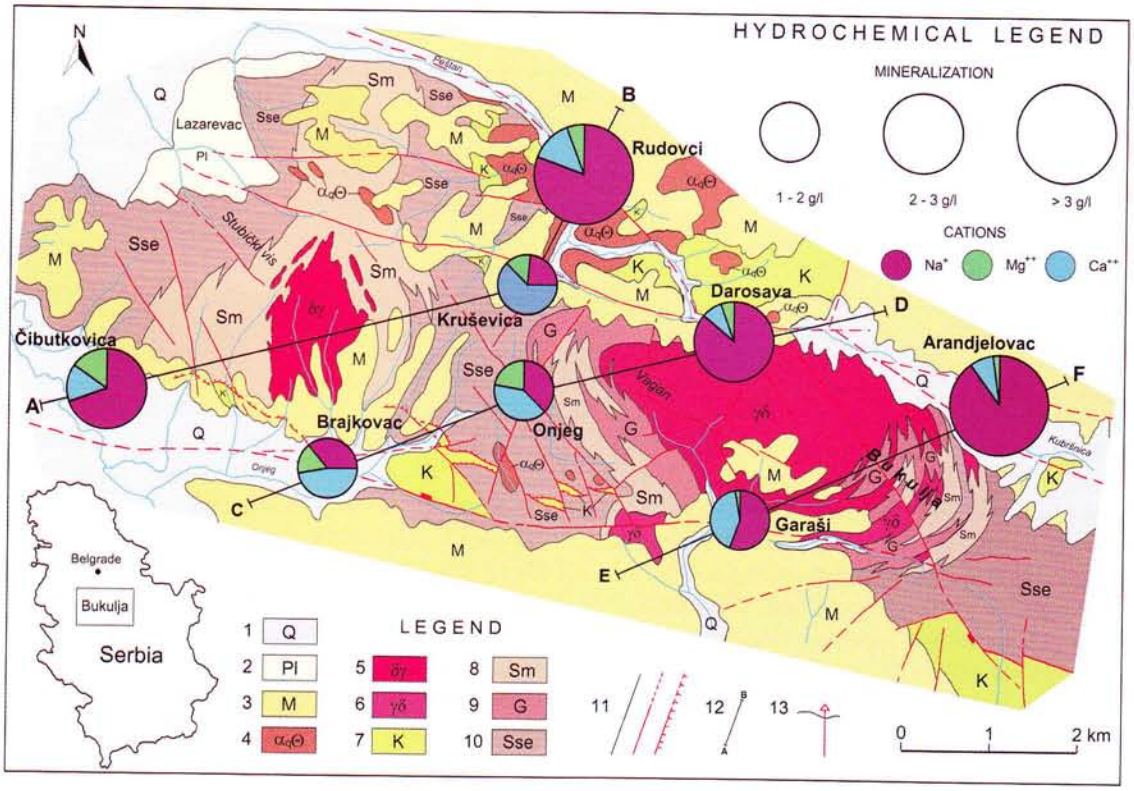

Fig. 1. Hydrochemical and geological map of the granitoid massif of Bukulja and Brajkovac, modified by I. Djoković and P. Papić, after: Basic geologic map, scale 1:100 000, sheets: Obrenovac (Filipović *et al.* 1979), Smederevo (Pavlović *et al.* 1979), Gornji Milanovac (Filipović *et al.* 1967) and Kragujevac (Brković *et al.* 1979). Legend: **1,** Quaternary sediments; **2,** Pliocene clastic sediments; **3,** Miocene conglomerate, sandstone and claystone; **4,** dacites, andesites and pyroclastic rocks; **5,** granitoid of Brajkovac; **6,** granitoid of Bukulja; **7,** Cretaceous flysch and limestones; **8,** mica schists; **9,** gneiss; **10,** sericite schists; **11,** contact and fault lines; **12,** geological cross section; **13,** borehole.

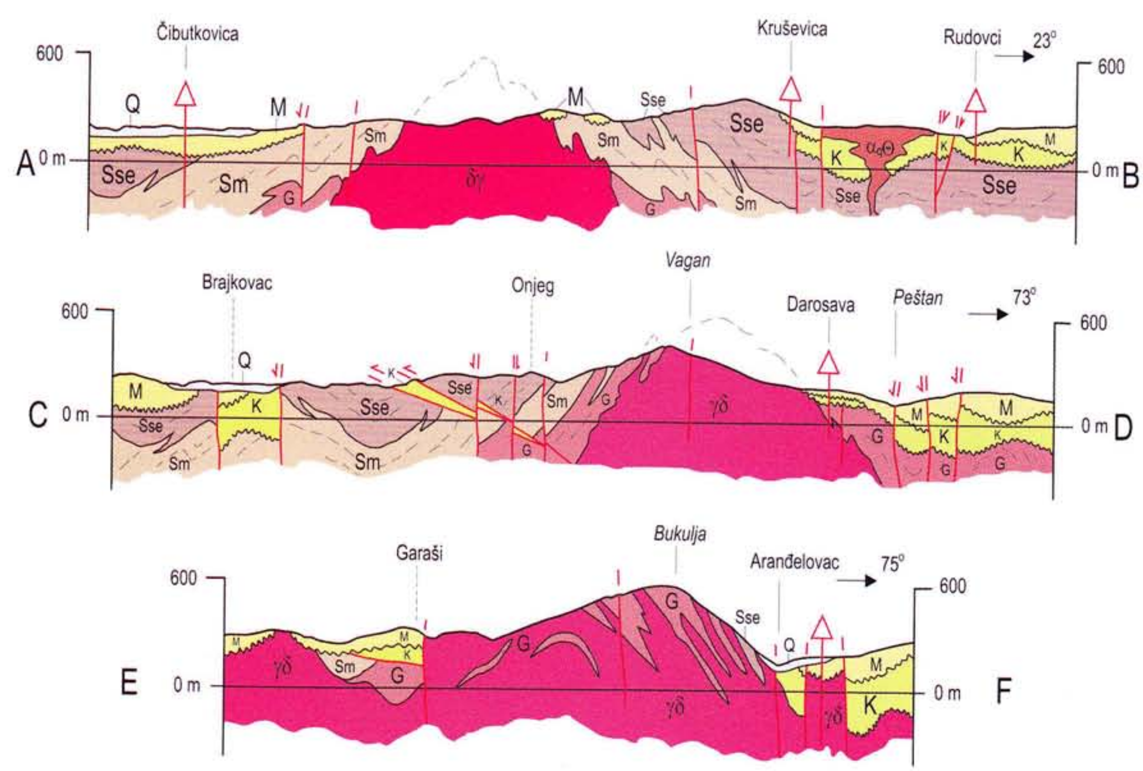

Fig. 2. Geological cross sections of the Bukulja and Brajkovac granitoid massifs (Legend is the same as for Fig. 1).

Table 1. Description of representative localities of carbonated mineral waters in the investigated area.

	Locality	*T* (°C)	Type of water source and depth of wells (m)	Flow rate (l/s)	Lithology
1	Čibutkovica	22.3	well (1002.8)	0.5	Paleozoic schist
2	Rudovci	18	well (119)	0.4	Paleozoic schist
3	Darosava	17.5	well (~50)	0.08	Granite
4	Arandjelovac	35.4	well (477)	2.2	Granite
5	Brajkovac	18.6	spring	0.03	Contact of Paleozoic schist and Cretaceous sediments
6	Onjeg	23	spring	0.02	Paleozoic schist and limestone
7	Garaši	16	spring	0.01	Paleozoic schist and Cretaceous sediments
8	Kruševica	22.1	well (65.5)	0.52	Sandy Tertiary sediments

particularly conspicuous in the vicinity of the investigated area (especially in the Venčac Mountain area) where masses of Cretaceous limestones were converted into marbles. The crystalline block base and its Cretaceous cover are overspread by Middle Miocene clastic rocks and pyroclastic rocks formed during the Miocene volcanic phases. Their intrusive and extrusive varieties in the form of dacite-andesites, phenoandesites and latites are widely spread in the northern part of the Bukulja block (along the Darosava–Rudovci–Kruševica–Lazarevac line), whereas in its southern part, they occur sporadically, near the headwater of the Onjeg River and in the form of erosion debris (DJOKOVIĆ & MARKOVIĆ 1986; DJOKOVIĆ & MARKOVIĆ 1985; KARAMATA 1994).

In the tectonic sense, the Bukulja block underwent a polyphase formation, which occurred during the Variscan and Alpine tectogenetic phases. Traces of Variscan folding are to be seen in rarely preserved portions of axial lines of folds and regionally developed axial-plane cleavage. During the Alpine tectogenenesis, the early structure of the Bukulja block was overfolded and it gained a different appearance. It is made of a large longitudinal antiform structure that resulted from overfolding of the Variscan cleavage. In their core, the pluton bodies of Bukulja and Brajkovac were embossed, which, by dome upfolding of the overlying rocks, partly altered the original fold form. The Alpine tectogenesis formed fault and joint structural fabrics, among which regional fractures are of crucial importance since they represent deep-seated faults in the Bukulja horst (TRIVIĆ 1998).

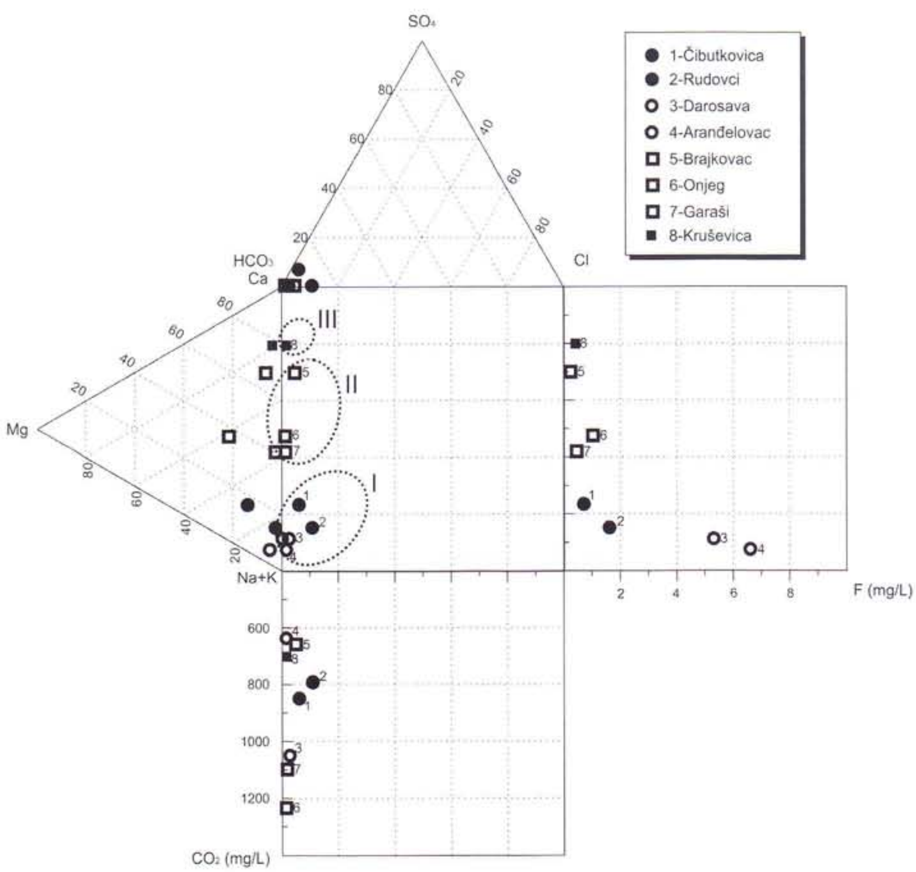

Fig. 3. Expanded Durov diagram with CO_2 and fluoride concentration (I, II and III – hydrochemical types of mineral waters).

Hydrogeochemistry

From the hydrochemical viewpoint, there are three types of mineral waters, as indicated on the Durov diagram (Fig. 3 I, II and III).

The first type is sodium hydrogencarbonate water (Čibutkovica, Rudovci, Darosava, Arandjelovac). They are mineral waters (*TDS* 1.7–3.8 g/L) with a carbon-dioxide content of 0.6–1.05 g/L. They have rather high contents of stron-

Table 2. Representative localities of carbonated mineral waters in the investigated area – macro and micro components.

	Locality	pH	CO_2 (mg/L)	*TDS* (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Cl (mg/L)	HCO_3 (mg/L)	SO_4 (mg/L)	SiO_2 (mg/L)	F (mg/L)	B (mg/L)	Li (mg/L)	Sr (mg/L)
1	Čibutkovica	6.27	853.6	1761.19	90.18	49.86	452	71	24.11	1568	89	57.8	0.7	1.14	2.39	2.83
2	Rudovci	6.53	792	3796.84	204.41	29.18	1443	78.6	283.6	4227	1	12.6	1.64	6.93	3.4	0.266
3	Darosava	6.27	1056	1713.82	70.14	0.73	641	46.8	26.23	1931.99	0.9	84	5.31	0.761	2.98	0.369
4	Arandjelovac	6.64	633.6	3524.5	60.12	41.34	1313	87.8	28.36	4046.74	3	84.1	6.62	1.02	6.05	1.27
5	Brajkovac	6.49	660	1582.39	400.8	26.75	188	11.5	44.67	1827.56	0.8	76.5	0.2	0.59	0.984	5.06
6	Onjeg	6.4	1230	3030	248.1	93	330	46.8	7.1	2165.5	0.5	120	1.0	0.2	2.88	2.65
7	Garaši	6.4	1100	2610	240.2	12.2	391	15.6	7.1	1836.1	2	100	0.4	0.5	2.85	2.1
8	Kruševica	6.32	704	1558.71	460.92	14.59	130	8.48	15.6	1853.67	0.9	112	0.36	0.08	0.746	2.19

tium, lithium, silicon and fluoride. The fluoride content ranges from 0.7 to 6.6 mg/L. Among other macrocomponents, it is worth mentioning the contents of calcium ions, which range from 60 to 204 mg/L. The values of the genetic coefficient, rNa/(rCa+rMg) (r is reacting concentration in % eqv.) range from 2.3 to 10. The mineral waters are genetically confined to Paleozoic schists and granite gneisses. The favorable migration of fluorides is affected by the slightly acid environment (pH around 6.5), carbon dioxide in gas composition, sodium hydrogencarbonate content and the relatively low calcium ion values (Table 2).

The second hydrochemical type of mineral waters are the sodium hydrogencarbonate-calcium waters (Garaši, Brajkovac and Onjeg), with high contents of strontium, lithium and silicon. The fluoride content ranges from 0.2 to 1 mg/L. Among macrocomponents in their chemical composition, the high calcium ion content, which range from 240 to 400 mg/L, is worth mentioning. The genetic coefficient values rNa/rCa+rMg range from 0.4 to 1.3. These mineral waters occur at the contacts of Paleozoic schists with Cretaceous sediments. As a result of the extremely high calcium values, the fluoride ion contents are an order of magnitude lower compared to the previous type of mineral water.

Third type of mineral water is calcium hydrogencarbonate water (Kruševica). The mineralization is about 1.55 g/L with a carbon dioxide content of about 0.7 g/L. This type has higher strontium and silica contents, but the contents of the other micro components are not elevated. The value of genetic coefficient rNa/Ca+Mg is about 0.3. The calcium content is extremely high and reaches 460 mg/L, consequently the fluoride ion contents are as low as 0.36 mg/L.

Discussion and conclusions

Correlation diagrams (Fig. 4) show positive correlation between the fluoride content and *TDS*, as well as between fluoride and the sodium content. It is also obvious from these diagrams that high concentrations of fluoride are present in waters with high values of the genetic coefficient (rNa/rCa+rMg). This was generally expected considering that decomposition processes of silicate and aluminosilicate minerals occur in the majority of these waters (in the presence of CO_2), resulting in a carbonated, sodium hydrogencarbonate composition of the water (Fig. 3).

Calcium ions are negatively correlated with fluoride ions, because the content of fluoride in water is limited by the solubility product of calcium fluoride (the more calcium, the less fluoride in water). It is obvious from the Fig. 4 that low fluoride concentrations (< 0.5 mg/L) appear in waters where the concentration of calcium ions are elevated (> 200 mg/L).

Saturation indexes (*SI*) of fluorite and calcite were calculated using chemical thermodynamics, and obtained values indicated mainly mineral waters unsaturated with respect to fluorite and oversaturated with respect to calcite (Table 3 and Fig. 4). There are two exceptions: the mineral water from Darosava, which is mildly saturated with respect to fluorite, and the mineral water from Arandjelovac, which is in equilibrium with fluorite. The fact that these two mineral waters differ from the rest of the analyzed waters could be observed on every correlation diagram – number 3 (Darosava) and number 4 (Arandjelovac) are always significantly separated from the rest of the symbols, *i.e.*, mineral waters, on the diagrams.

The fact that the majority of analyzed waters are unsaturated with respect to fluorite is explained by the elevated concentrations of calcium (and consequently low concentrations of fluoride). The conclusion is that precipitation of fluorite is not possible under these hydrochemical conditions.

By comparing geological and tectonic characteristics and results of hydrochemical research, it was established that there is an evident connection between geological structure of the Bukulja substrate and the hydrocarbonate mineral water genesis. It was concluded that, apart from lithology, joint fabrics and larger dislocation structures are of crucial importance for the water chemistry in the studied region. In addition, it should be stated that smaller ruptures determine the type of porosity that enables the accumulation of groundwater in the rock mass and its chemical transformation, while larger dislocation forms determine the stream flows of the regional water circulation. For better perception of the correlation between certain spring

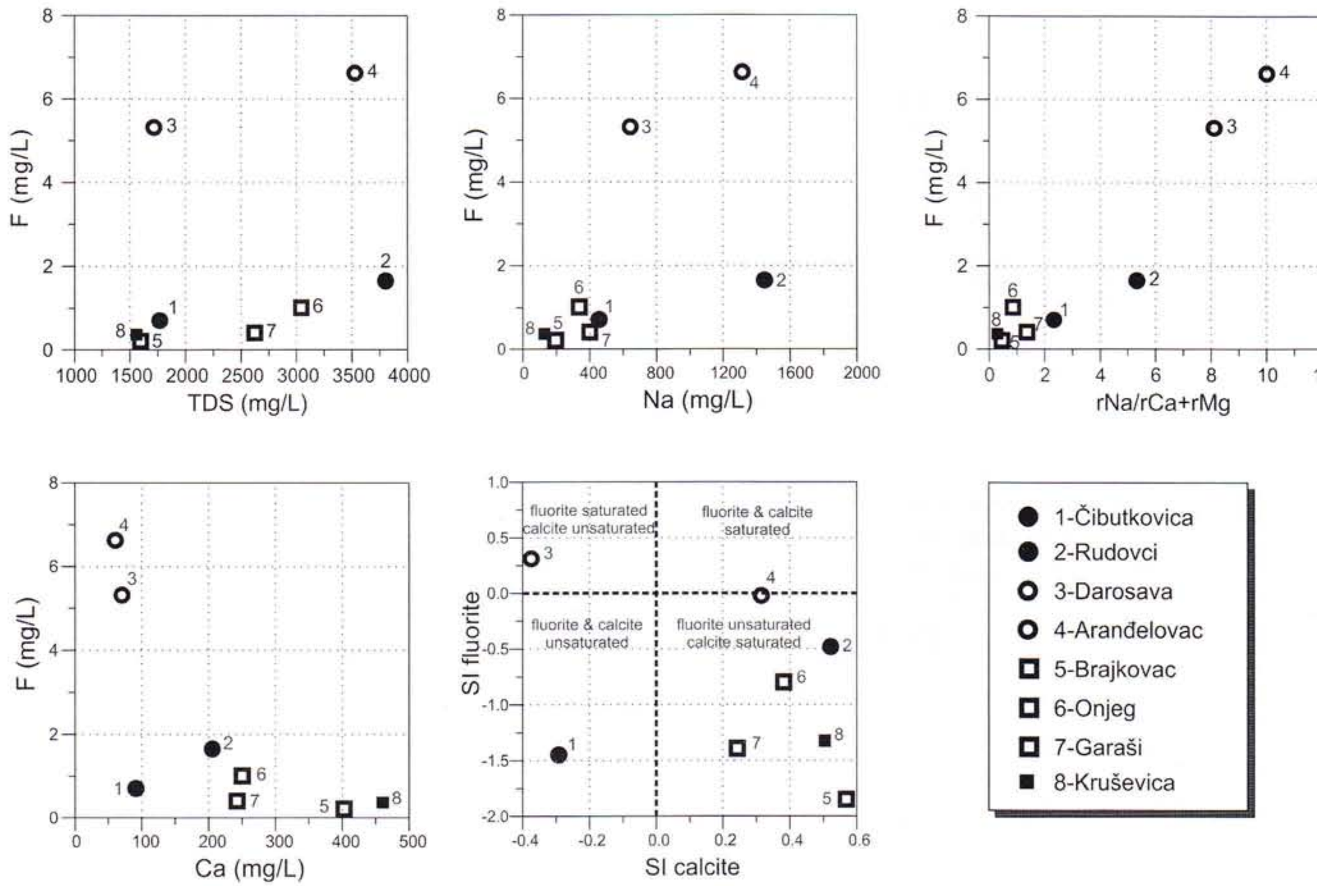

Fig. 4. Correlation diagrams for selected hydrochemical parameters.

Table 3. Representative localities of carbonated mineral waters in the investigated area – water type, genetic coefficients and saturation indexes (*SI*).

	Locality	Water type	*r*Na/*r*Ca+*r*Mg (r, %eqv)	*SI* calcite	*SI* fluorite
1	Čibutkovica	HCO_3-Na	2.3	-0.29	-1.45
2	Rudovci	HCO_3-Na	5.3	+0.52	-0.49
3	Darosava	HCO_3-Na,	8.1	-0.38	+0.31
4	Arandjelovac	HCO_3-Na,	10.0	+0.31	-0.02
5	Brajkovac	HCO_3- Na, Ca	0.4	+0.56	-1.85
6	Onjeg	HCO_3-Ca, Na,Mg	0.8	+0.38	-0.80
7	Garaši	HCO_3-Ca, Na	1.3	+0.24	-1.40
8	Kruševica	HCO_3-Ca	0.3	+0.51	-1.33

areas, a hydrochemical map was constructed with major geological structures along with hydrochemical properties of the spring locations (Fig. 1).

In order to present clearly the correlation between geological and hydrochemical parameters, transversal and diagonal cross sections were drawn, displaying the basic structures and lithologic properties of the rocks (Fig. 2). Associated with them are the following spring areas:

– Čibutkovica–Kruševica–Rudovci
– Brajkovac–Onjeg–Darosava and
– Garaši–Arandjelovac

In accordance with previous conclusions, it was established that the main spring areas of sodium hydrogencarbonate mineral waters (having dominant sodium content) occur along the complex regional fault which borders the Bukulja block on its north-eastern side, whereas mineral waters with dominant calcium content appear along the dislocation which borders its northern side.

It is obvious that the north-eastern dislocation (which connects Arandjelovac, Darosava and Rudovci) and the sets of joints that accompany it cut muscovite granite, gneiss, igneous and clastic flysch rocks, which in turn influence the formation of sodium waters.

In the spring area of Čibutkovica, the hydrogencarbonate mineral waters have distinctly sodium characteristics, which prove that the southern dislocation does not act as a groundwater recharge. Recharge is most probably realized in the metamorphic complex that forms the northern hinterland of the spring area.

In contrast, along the southern dislocation, Bukulja crystalline rocks are at many places in contact with

Upper Cretaceous clastic-carbonate flysch, which increases the amount of calcium in the spring areas of Garaši and Brajkovac. The Onjeg locality belongs to this group, its water having a higher content of calcium due to the dissolution of the limestone thick layers that form a tectonic block between the two reverse faults.

The water of Kruševica spring is characterized by a high content of calcium, but the contents of the micro components are not elevated, except for strontium and silica. This is due to a shallower zone of groundwater formation in the sandy Tertiary sediments.

It should be emphasized that the two mineral waters belonging to the first type are bottled as the mineral water "Knjaz Miloš" from Arandjelovac (Bukovička spa) and "Dar voda" from Darosava. The fluoride concentrations in these waters are higher than 1 mg/L; hence, they are called fluoride waters. Due to the biological activity of fluoride, its content is limited to 5 mg/L for bottled mineral waters. If the level is higher than 1.5 mg/L, the term "contains more than 1.5 mg/L of fluoride: not suitable for regular consumption by infants and children under 7 years of age" should appear on the label in close proximity to the name of the product. The European Directive on the exploitation and marketing of natural mineral waters and spring waters sets standards for excluding harmful elements such as fluoride ions, iron, manganese, sulfur and arsenic. It is obvious from the obtained results that some mineral waters in Serbia should be subjected to water treatment, which seems to be difficult in practice, and sometimes nature itself plays the role of a "technologist". Two possibilities are offered here: the right choice of locations for abstraction of mineral water with satisfactory chemical composition, which is a hydrogeologist's task, and the application of artificial defluoridization by means of aluminum oxide, lime, ion exchange resins or similar methods, which is a technologist's task. It is important to emphasize the impact and application of hydrochemical methods throughout hydrogeological research, which includes defining the conditions and factors of migrations of fluoride ions in mineral waters, the defining of the basic hydrochemical types of waters with high and low levels of ions and of gas composition, as well as the thermodynamic conditions in aquifers with accumulated mineral waters.

Acknowledgments

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References

Bailey, J.C. 1977. Fluorine in granitic rocks and melts: A review. *Chemical Geology*, 19 (1–4): 1–42.

Brković, T., Radovanović, Z. & Pavlović, Z. 1979. *Explanatory book for the basic geologic map, scale 1:100 000, sheet Kragujevac*. Federal Geologic Survey, Belgrade (in Serbian, English summary).

Djoković, I. & Marković, M. 1985. Characteristics of Bukulja crystalline. *Bulletin of the Serbian Geological Society*, Belgrade, 35–37 (in Serbian).

Djoković, I. & Marković, M. 1986. Polyphase forming of Bukulja crystalline complex. *11th Geological Congress of Yugoslavia*, Book of Abstracts, 3: 293–298 (in Serbian).

Filipović, I., Pavlović, Z., Marković, B., Radin, V., Marković, O., Gagić, N., Atin, B. & Milićević, M. 1967. *Explanatory book for the basic geologic map, scale 1:100 000, sheet Gornji Milanovac*. Federal Geologic Survey, Belgrade (in Serbian, English summary).

Filipović, I., Radin, V., Pavlović, Z., Milićević, M. & Atin, B. 1979. *Explanatory book for the basic geologic map, scale 1:100 000, sheet Obrenovac*. Federal Geologic Survey, Belgrade (in Serbian, English summary).

Fordyce, F.M. 2011. Fluorine: human health risks. *In*: Nriagu, J.O. (ed.), *Encyclopedia of Environmental Health*, 2: 776–785, Elsevier, Burlington.

Furi, W., Razack, M., Abiye, T.A., Ayenew, T. & Legesse, D. 2011. Fluoride enrichment mechanism and geospatial distribution in the volcanic aquifers of the Middle Awash Basin, Northern Main Ethiopian Rift. *Journal of African Earth Sciences*, 60 (5): 315–327.

Hitchon, B., Perkins, E.H. & Gunter, W.D. 1999. *Introduction to Ground Water Geochemistry*. 310 pp. Geoscience Publishing Ltd., Alberta, Canada.

Karamata, S., Vasković, N., Cvetković, V. & Knežević, V. 1994. Upper Cretaceous and Tertiary magmatites of central and eastern Serbia and their metallogeny. *Geološki anali Balkanskoga poluostrva*, 58 (1): 165–181 (in Serbian).

Kim, K. & Jeong, G.Y. 2005. Factors influencing natural occurrence of fluoride-rich groundwaters: a case study in the southeastern part of the Korean Peninsula. *Chemosphere*, 58: 1399–1408.

Papić, P. 1994. Migration of fluorine in mineral waters of Serbia. 132 pp. Unpublished MSc thesis, Faculty of Mining and Geology, University of Belgrade (in Serbian).

Pavlović, Z., Marković, B., Atin, B., Dolić, D., Gagić, N., Marković, O., Dimitrijević, M. N. & Vuković M. 1979. *Explanatory book for the basic geologic map, scale 1:100 000, sheet Smederevo*. Federal Geologic Survey, Belgrade (in Serbian, English summary).

Rafique, T., Naseem, S., Usmani, T.H., Bashir, E., Khan, F.A. & Bhanger, M.I. 2009: Geochemical factors controlling the occurrence of high fluoride groundwater in the Nagar Parkar area, Sindh, Pakistan. *Journal of Hazardous Materials*, 171: 424–430.

RANKAMA, K. & SAHAMA, T.G. 1950. *Geochemistry*. 928 pp. The University of Chicago Press, Chicago.

REDDY, D.V., NAGABHUSHANAM, P., SUKHIJA, B.S., REDDY, A.G.S. & SMEDLEY, P.L. 2010. Fluoride dynamics in the granitic aquifer of the Wailapally watershed, Nalgonda District, India. *Chemical Geology*, 269: 278–289.

SEELIG, U. & BUCHER, K. 2010. Halogens in water from the crystalline basement of the Gotthard rail base tunnel (central Alps). *Geochimica Cosmochimica Acta*, 74: 2581–2595.

SHAJI, E., BINDU, VIJU, J. & THAMBI, D.S. 2007. High fluoride in groundwater of Palghat District, Kerala. *Current Science*, 92 (2): 240–245.

SREEDEVI, P.D., AHMED, S., MADE, B., LEDOUX, E. & GANDOLFI, J.M. 2006. Association of hydrogeological factors in temporal variations of fluoride concentration in a crystalline aquifer in India. *Environmental Geology*, 50: 1–11.

TIRUMALESH, K., SHIVANNA, K. & JALIHAL, A.A. 2007. Isotope hydrochemical approach to understand fluoride release into groundwaters of Ilkal area, Bagalkot District, Karnataka, India. *Hydrogeology Journal*, 15: 589–598.

TRIVIĆ, B. 1998. Tectonic structure of metamorphic edge of Bukulja granodiorite. 170 pp. Unpublished PhD dissertation, Faculty of Mining and Geology, University of Belgrade (in Serbian).

US National Research Council, Committee on Fluoride in Drinking Water (2006). Fluoride in Drinking Water: A Scientific Review of EPA's Standards. National Academies Press, Washington D.C., pp. 187, 223, 249.

Резиме

Утицај геологије на миграцију флуорида у минералним водама околине плутона Букуље и Брајковца, Србија

Хидрохемијска истраживања вода ширег подручја Букуљског и Брајковачког плутона су обављена ради утврђивања њихових хемизама и генетских својстава. Испитивањима је обухваћено осам најважнијих извориштних локалитета, од којих се Аранђеловац, Даросава и Рудовци налазе на североисточном, Гараши, Брајковац и Чибутковица у југозападном, а Оњег и Крушевица у централном делу изучаваног простора. Пошто су хидрохемијске анализе указале да је у наведеним извориштима присутно варирање хемизма вода, било је очигледно да су за разјашњавање њихове генезе, поред хидрохемијских истраживања, неопходна и изучавања регионалне грађе. Ради тога су извршени и додатани геолошки радови, што је у целини створило основу за тумачење генезе хидрокарбонатних вода.У тектонском смислу букуљски блок је претрпео полифазна обликовања, која су се одиграла током варисцијске и алпске тектонске фазе. Трагови варисцијског набирања се манифестују кроз ретко сачуване делове набора и регионално развијен кливаж аксијалне површине. Током алпске тектогенезе ранија структура букуљског блока је пренабирана, при чему је стекла другачији изглед. Њу чини крупна лонгитудинална антиформна структура, настала пренабирањем варисцијског кливажа. У њен језгрени део су утиснута плутонска тела Букуље у Брајковца, која су куполастим задизањем кровине донекле изменила основну наборну форму. Алпским обликовањима су формирани раседни и пукотински склопови, од којих посебан значај имају регионални разломи који представљају кључне граничне структуре букуљског хорста.

Следећи претходне закључке, утврђено је да се главна изворишта хидрокарбонатно-натријумских вода (са доминантном натријумском компонентом) јављају на сложеном регионалном раседу који ограничава букуљски блок са североисточне стране, а да се на дислокацији која га ограничава са југа јављају воде са доминантним јоном калцијума. Очигледно је да североисточна дислокација (која повезује изворишта Аранђеловца, Даросаве и Рудоваца) и пукотински системи који се налазе уз њу, у највећој мери пресецају гранитмонцонитске, гнајсне, вулканске и кластичне флишне стене, које својим саставом утичу на формирање натријумског типа воде.

Насупрот томе, јужна гранична дислокација на више места гради контакт између букуљског кристалина и горњокредног кластично-карбонатног флиша, што доприноси повећању калцијума у извориштним подручијима Гараши и Брајковац. У ову групу изворишта треба сврстати и локалност Оњег, чија вода има повећан садржај калцијума, што је највероватније последица растварања кречњачких пакета, који граде тектонске пласа, укљештене између два реверсна раседа. У извориштна подручја Чибутковице хидрокарбонатне воде имају изразито натријумски карактер, што показује да у овом изворишту јужна гранична дислокација нема функцију прихрањивања. Подручје се вероватно прихрањује из метаморфног комплекса који чини северну залеђину изворишта. Извориштна област Крушевице представља хидрогеолошки загонетну појаву. У њеним водама изразито доминира калцијум, мада се сам локалитет налази у зони гнајсних стена. Изгледа да се у северној околини изворишта, испод миоценских седимената налази остатак трансгресивних, флишних седимената, а у њима се често јављају банци песковитих кречњака. Могуће је да су они дали калцијумску компоненту води.