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.

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, 1980).
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 (TIRUMALESHE 2006; SHAJI 2007) and there is a strong correlation between the lithology of aquifers and the fluoride concentration in groundwater (SEELEG 2010). Relevant fluoride minerals are: amphibole, mica, fluorite (CaF2), apatite (Ca5(PO4)3(F,OH,Cl)), topaz (Al2SiO4(F,OH)2) and cryolite (Na3AlF6). 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 Ca2+ 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 Ca2+ 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 Brjakovac 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 Brjakovac 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 phylite, 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 basalt clastic limestones and flysch sediments, which in the course of intrusion of the Bukulja granite monzonite and the Brjakovac granodiorite, underwent some contact metamorphic changes. These are
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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 (FILIPOVIC et al. 1979), Smederevo (PAVLOVIĆ et al. 1979), Gornji Milanovac (FILIPOVIC et al. 1967) and Kragujevac (BRKOVIC 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).
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, pheno-andesites 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 tectogenesis, 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).

**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 (Čibuktkovica, 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-
tium, lithium, silicon and fluoride. The fluoride con-
tent ranges from 0.7 to 6.6 mg/L. Among other macro-
components, it is worth mentioning the contents of
calcium ions, which range from 60 to 204 mg/L. The
values of the genetic coefficient, $r_{Na}/(r_{Ca}+r_{Mg})$ ($r$ 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 (Ga-
raši, Brajkovac and Onjeg), with high contents of stron-
tium, 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 mention-
ing. The genetic coefficient values $r_{Na}/r_{Ca}+r_{Mg}$ range
from 0.4 to 1.3. These mineral waters occur at the con-
tacts 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 hydrogen-
carbonate 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 con-
tents, but the contents of the other micro components
are not elevated. The value of genetic coefficient
$r_{Na}/Ca+Mg$ is about 0.3. The calcium content is ex-
tremely 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 correla-
tion 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 $(r_{Na}/r_{Ca}+r_{Mg})$. 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 fluo-
ride 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 concentra-
tions (< 0.5 mg/L) appear in waters where the concen-
tration of calcium ions are elevated (> 200 mg/L).

Saturation indexes ($SI$) of fluorite and calcite were
calculated using chemical thermodynamics, and ob-
tained values indicated mainly mineral waters unsatu-
rated 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 equilib-
rium 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 characteris-
tics 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 addi-
tion, 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 transfor-
mation, while larger dislocation forms determine the
stream flows of the regional water circulation. For bet-
ter perception of the correlation between certain spring

<table>
<thead>
<tr>
<th>Locality</th>
<th>pH</th>
<th>CO$_2$ (mg/L)</th>
<th>TDS (mg/L)</th>
<th>Ca (mg/L)</th>
<th>Mg (mg/L)</th>
<th>Na (mg/L)</th>
<th>K (mg/L)</th>
<th>Cl (mg/L)</th>
<th>HCO$_3$ (mg/L)</th>
<th>SO$_4$ (mg/L)</th>
<th>SiO$_2$ (mg/L)</th>
<th>F (mg/L)</th>
<th>B (mg/L)</th>
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<td>49.86</td>
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<td>1443</td>
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<td>1713.82</td>
<td>70.14</td>
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<td>641</td>
<td>46.8</td>
<td>26.23</td>
<td>1931.99</td>
<td>0.9</td>
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<td>5.31</td>
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<td>1582.39</td>
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<td>11.5</td>
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<td>3030.0</td>
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<td>2610.0</td>
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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.

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References

Српски језик

Резиме

Утицај геологије на миграцију флуорида у минералним водах

Хидрокемијска истраживања вода ширег подручја Букуљског и Брајковачког плутона су обављена ради утврђивања њихових хемизама и генетских својства. Испитивањима је обухватао осам најважнијих изворишта хидрокарбонатно-натријумских вода у изворишним подручјима Гараши и Брајковац. У овај букуљски хорст налазе се многи реверсни раседови, који представљају кључне граничне структуре, које посебан значај имају регионалним разламовима и миграцијом флуорида у минералним водах. У тектонском смислу букуљски блок је претрпео полицифарну обликованост, што је се одиграло током варицијске и алиске тектонске фазе. Трагови варицијског набирана се манифестују кроз ретко сачуване делове набора и регионално развијени кивав аксијалне површине. Током алиске тектогенезе ранија структура букуљског блока је препознана, али њен језгрени део је стекла својствена структура, која је ћеловеком заточена мегаслонасе и мегаслонасны системи који су јужни главни спречив још изворишта Аранђеловца, Даросаве и Рудоваца, као и јужни системе који се налазе у њу, у највишој мери пресецај претрпео гранит-монцонитске, њежене вулканске и кластичне флишне стена, које својим саставом утичу на формирање и додатно геолошке радови, што је сенача јасти претрцео тектонски одрасло у највишем подручју. Миграција флуорида у минералним водах је установљена у зони северно-источне гранит-монцонитске аномале. Насупрот томе, јужна гранитна дислокацija јавља се на сложеном регионалном раседу који ограничава букуљски блок са јужном границом. Флуорид је укупна гранит-монцонитска, њежена вулканска и кластична флишна стена, које својим саставом утичу на формирање букуљског хорста.

Следећи претходне закључке, утврђено је да се главна изворишта хидрокарбонатно-натријумских вода са јужном границом регионалног раседа који ограничава букуљски блок са јужном границом. Флуорид је укупна гранит-монцонитска, њежена вулканска и кластична флишна стена, које својим саставом утичу на формирање букуљског хорста. Насупрот томе, јужна гранитна дислокацija јавља се на сложеном регионалном раседу који ограничава букуљски блок са јужном границом. Флуорид је укупна гранит-монцонитска, њежена вулканска и кластична флишна стена, које својим саставом утичу на формирање букуљског хорста.

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