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Hydrogeochemistry of thermal groundwaters in the Serbian crystalline core region

Tanja Petrović Pantić [a],*, Manfred Birke [b], Branislav Petrović [c], Jovana Nikolov [d], Veselin Dragišić [c], Vladimir Živanović [c]

[a] Geological Survey of Serbia, 12 Rovinjska Street, 11000 Belgrade, Serbia
[b] Federal Institute for Geoscience and Natural Resources, 2 Stilleweg, 20655 Hannover, Germany
[c] University of Belgrade, Faculty of Mining and Geology, 7 Djusina Street, 11000 Belgrade, Serbia
[d] University of Novi Sad, Faculty of Sciences, Department of Physics, 4 Dositej Obradovic Square, 21000 Novi Sad, Serbia

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ABSTRACT

Geochemical exploration has been applied for studying thermal groundwater characteristics in the Serbian crystalline core region. Within this hydrogeological region, thermal groundwater with temperature higher than 20 °C occurs at seven locations. The maximum discharge temperature of the thermal groundwater is 105 °C which is the highest groundwater temperature encountered in Serbia. Geothermal reservoirs are present within andesite, schist, grus (the fragmental products of in-situ granular disintegration granite), marl and sandstone. Based on the concentrations of the major elements all of the water samples are of HCO_3–Na to SO_4–Na type. An elevated content of F, B, Ge and Rb is observed, while some samples also exhibit higher concentrations of As, Be, Cs, Ga, Ge, Li, V and W, and one has elevated concentrations of Nb, Zr and heavy rare earth elements (HREE). The groundwater is neutral to alkaline with TDS of 130–3822 mg/L.

Making use of various geothermometers, it was estimated that the temperatures in the selected aquifers of the Serbian crystalline core range from 45 to 146 °C.

Activity concentration of ^{222}Rn ranges from 10.4 ± 0.9 to 104 ± 15 Bq/L and is higher in groundwater that is in contact with schist and along faults, while ^{226}Ra has a smaller activity concentrations, within the range of 0.21 ± 0.09 to 0.48 ± 0.18 Bq/L.

1. Introduction

Previous research on thermal groundwater in the Serbian crystalline core region has been mostly focused on the characterization and study of the geothermal resources, with stable quality and temperature (Stanković, 1988; Stanković and i Zlokolica, 1993; Zlokolica et al., 1994; Zlokolica and Ilić, 1994; Milovanović, 2001; Špadijer et al., 2005; Tasić, 2006; Jovanović, 2008; Milanović, 2009). The characteristics of these groundwaters are also discussed in other studies (Milovanović, 1992; Protić, 1995; Milivojević and Perić, 1990; Filipović, 2003).

There are six hydrogeological regions in Serbia (Filipović et al., 2005): the Dacian basin region, the Carpatho-Balkan Mts. region, the Serbian crystalline core region, the Šumadija–Kopaonik–Kosovo region, the Internal Dinarides region of western Serbia and the Pannonian basin region.

The Pannonian basin extends in the northern part of Serbia, where 78 geothermal wells exist (Martinović et al., 2010); in other regions of Serbia there are a number of natural thermal springs. Most of the thermal springs and wells (temperature > 20 °C) are found in carbonate aquifers under deep layers of Neogene sediments (Pannonian basin and Internal Dinarides–Mačva). The highest groundwater temperatures are measured in samples extracted from igneous, metamorphic and contact-metamorphic rocks of the Serbian crystalline core.

Thermal groundwater in the Serbian crystalline core (henceforth referred to as the SCC) region has been encountered so far at seven locations namely Ribarska Banja, Prolom Banja, Sijarinska Banja, Viča, Tulare, Vranjska Banja and Bujanovačka Banja (Fig. 1). Five locations have spa status, while at two locations (Viča and Tulare), groundwater with temperatures ranging from 23 to 26 °C, is used by the local population. Water in spas is mostly used for balneotherapy and for recreation, while in some cases thermal water is either bottled (wells: P2, B4 and B5), or used for other beneficial uses such as for water supply (Prolom Banja), for heating of spa buildings (at Ribarska Banja, Sijarinska Banja and Vranjska Banja) or for heating greenhouses (Vranjska Banja).

Prolom Banja is located on the northern slopes of Mt. Radan at an elevation of 630 m and is the spa with the highest elevation in Serbia. The geothermal reservoir of Prolom Banja is within the Lece andesite massif, with an area of 700 km^2 and volcanic activity during the Tertiary (Malešević et al., 1974). Thermal water (temperature from 30 to 33 °C) is taken from two wells (depths of 160 and 500 m) drilled into the andesite aquifer.

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* Corresponding author.
E-mail address: tanjapetrovic.hg@gmail.com (T.P. Pantić).

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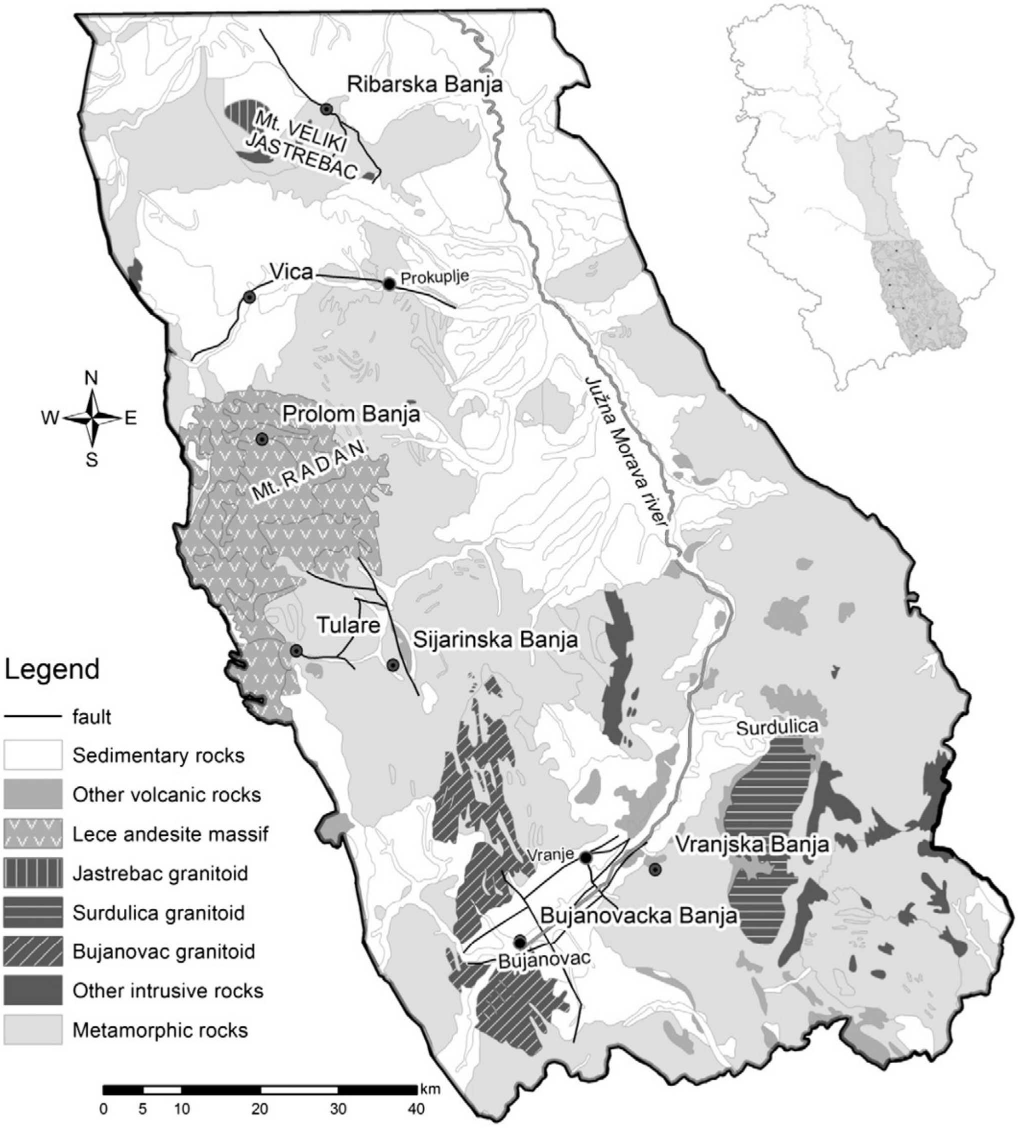

Fig. 1. Geological map of the lower part of Serbian crystalline core and the locations of thermal groundwater (only major faults in the study area are shown on the map). Sampling points are very close at each spa location, so it is impossible to be shown on map.

Ribarska Banja is located on the eastern hillsides slopes of Mt. Veliki Jastrebac, at an elevation of 540 m. This mountain was formed by the intrusion of a granitoid into Upper Cretaceous–Paleogene metamorphic rocks. These rocks (phylite, metasandstone, metasiltstone, conglomerate and contact-metamorphic rocks) are overthrusted by high-grade schists. Groundwater temperature ranges between 38 °C and 54 °C. Water is extracted from contact-metamorphic rocks of Jastrebac granitoid by wells with depths of 163 to 1543 m.

The thermal water at Sijarinska Banja is extracted from a shallow well with a depth of 8 m (71 °C, S2 in Table 2), as well as from a deep well with depth of 1232 m depth (76 °C, S3 in Table 2). The terrain mainly comprises crystalline rock, e.g., gneiss, leptinolite and mica–schist, with andesite outcrops. The most significant heat conductor is a large fault zone that connects the Sijarinska Banja and the Lece andesite massif.

The maximum recorded groundwater temperature at Vranjska Banja is 105 °C (in well VG-3). The Surdulica granodiorite, which contains numerous dykes of quartz latite and dacite, is present on the southeastern side of the spa, while andesite–dacite–volcanic necks are found on the western side — evidence for intense volcanic activity during the Tertiary. These activities resulted in the formation of a succession of volcanogenic-sedimentary rocks, of Miocene to the Pliocene age. The rocks underlying these magmatic rocks at Vranjska Banja are metamorphic (granite gneiss, gneiss and amphibolites). Based on a hydrodynamic test and a mathematical simulation model (Zlokolica et al., 1994; Martinović and Magazinović, 2010), about 100 L/s of the groundwater of Vranjska Banja can be sustainably utilized. This spa has the highest geothermal potential in Serbia.

Bujanovačka Banja is located in a valley that is surrounded by Bujanovac granitoid. The Bujanovac basin comprises of alluvial Neogene sediments on surface, underlain by Miocene sandstones, conglomerates and marls and the Hercynian granite and grus bedrock (Petrović et al., 2012). Temperatures of groundwater range from 29 °C (water extracted from marl and sandstone) to 46 °C (water extracted from grus).

The Tulare village is located 15 km west of Sijarinska Banja, on the southeastern part of the Lece andesite massif. The geological sequence comprises Tertiary rocks, volcaniclastic rocks composed of andesite, tuffs and pyroclastic breccia and subvolcanic diorite rocks that unconformably overlay the metamorphic base rocks. The metamorphic base rocks, especially the Fe-rich varieties, are hydrothermally altered and mineralized. Well T1, for instance, with a groundwater temperature of 26 °C, was drilled through hydrothermally altered rocks to the depth of 300 m.

In the village Viča, groundwater with a temperature of 19 °C was encountered within gneiss (wells depths from 10 to 20 m). The well VC in Viča, with groundwater temperature of 23 °C, was drilled through gneiss and marble to the depth of 107 m.

2. Geological and hydrogeological settings

The hydrogeological region of the SCC belongs to a large extent to the geotectonic unit of the Serbo-Macedonian Massif (according to Dimitrijević, 1994, see Petrović et al., 2010). It is mostly composed of high to medium-grade meta-igneous and meta-sedimentary rocks, such as gneiss, micaschist, amphibolite, amphibole–biotite schist, amphibole–pyroxene schist with sporadic occurrence of marble and migmatites.

Various granitoids have penetrated the SCC mostly along major faults comprising: the Vlajna granitoids (Early Paleozoic), the Bujanovac granitoid (Variscan orogeny — Late Paleozoic) and Tertiary granitoids: the Surdulica granodiorite (Oligocene) and the Jastrebac granitoid (Eocene) and their volcanic equivalents, andesite, dacite and tuff (the Lece andesite massif, the area of the Surdulica granodiorite, the area surrounding Vranje).

Tertiary deposits are distributed mainly in the northern and central parts of the SCC region, while Quaternary sediments are predominantly present along major rivers and streams.

Thermal water occurs within the southern part of the SCC (Figs. 1 and 2). The temperatures of water in Prolom Banja, Ribarska Banja, Sijarinska Banja, Vranjska Banja and Bujanovačka Banja range between 30 and 100 °C. Lower temperatures are observed in the water from wells drilled at Viča (23 °C) and Tulare (26 °C). The groundwater with the highest temperatures is associated with Tertiary magmatism. Tertiary magmatism in this area is divided into a Late Paleogene/Early Neogene granitoid, a Dinaridic granitoid suite and a volcanic formation in the Paleogen/Neogene central part of the Balkan peninsula with medium to high-K calc–alkaline rocks (Cvetković et al., 2000). Heat flow in this area is above 100 mW/m^2 (Milivojević et al., 1992; Martinović and Milivojević, 2010), in deep wells in Vranjska, Sijarinska and Ribarska Banja, heat flow is in range from 136 to 191,5 mW/m^2 (Petrović Pantić, 2014).

Groundwater is extracted from andesite (Prolom Banja), andesite and gneiss (Sijarinska Banja, Tulare), gneiss (Vranjska Banja), schist (Ribarska Banja, Viča), granites and grus (Bujanovačka Banja, spring B1, wells B2 and B3) and marl and sandstone (Bujanovačka Banja, wells B4 and B5).

From the hydrogeological aspect, the following types of aquifers are present in the SCC region: an intergranular aquifer, with low, medium and high permeability, a fractured aquifer, a karst-fractured aquifer and a complex aquifer system with all three of these types of aquifers (Fig. 2).

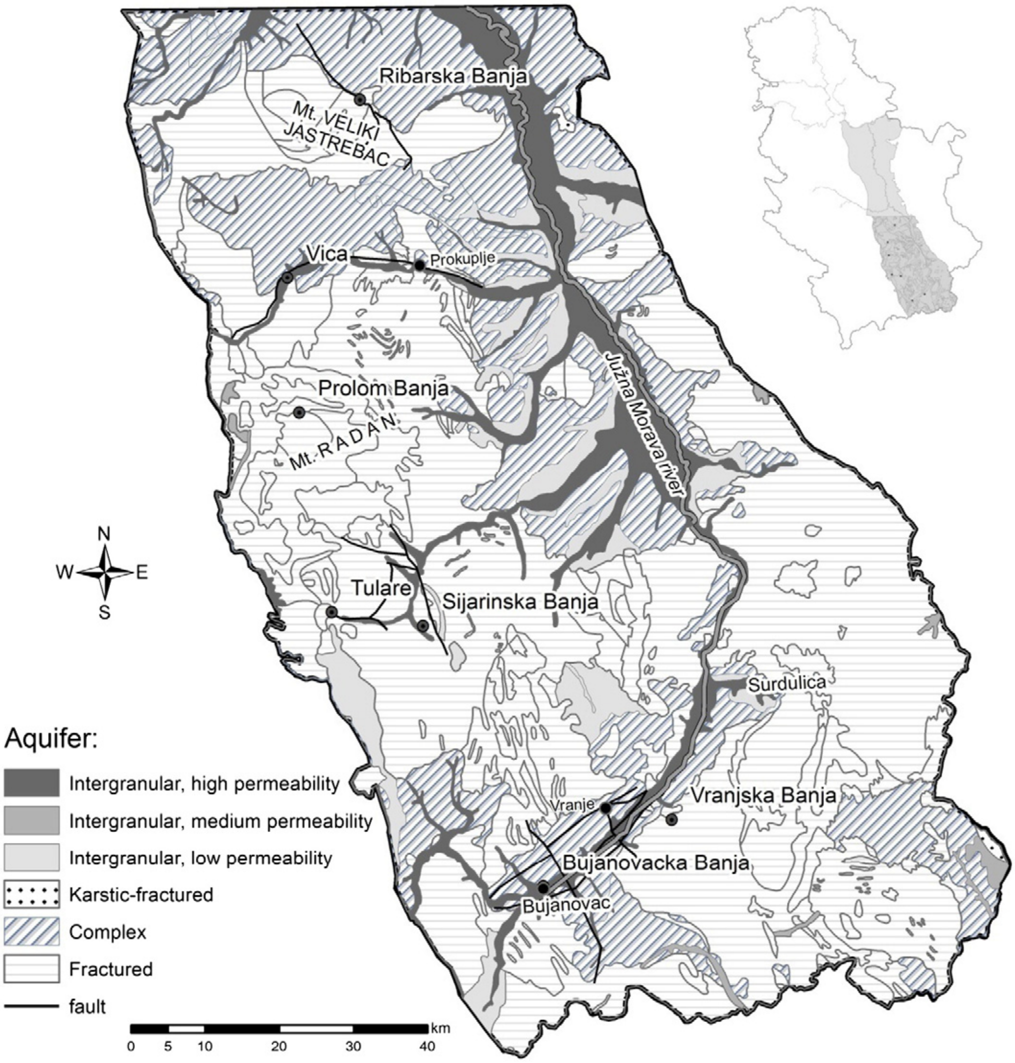

Fig. 2. Hydrogeological map of the lower part of the Serbian crystalline core and locations of thermal groundwater.

The intergranular aquifer does not have large area extent. It is present in the Bujanovac basin and is made up of grus. Due to the presence of conglomerate and breccia with fragments of granite this aquifer is characterized by intergranular-fracture porosity.

The fractured aquifer has vast distribution over the granites, granodiorites (Surdulica), andesites (Prolom Banja), as well as within the upper unit of semi-metamorphosed and non-metamorphosed clastic rocks, such as phyllite, metasandstone, metasiltstone, conglomerate, sandstone (Ribarska Banja).

The karst-fractured aquifer appears in marble, calc–schist and marbleized limestone, with small area of distribution. It is the main groundwater environment at Viča (VC).

The complex aquifer system consists of sand, sandstone with marl and shale in Bujanovačka Banja (wells B4 and B5). A complex aquifer is also present at Vranjska Banja and Sijarinska Banja consisting of crystalline rocks (gneiss, leptinolite, micaschist, amphibolite) which are more or less tectonically deformed, with a number of faults. Also groundwater at Tulare is formed within a complex aquifer with volcaniclastic rocks together with andesite and gneiss.

3. Methods

Chemical analyses were carried out on 18 samples of thermal groundwater and one sample of nonthermal (fresh) groundwater during 2011 (Table 1). Nonthermal groundwater was sampled from the granitoid spring in Bujanovac because it is the only water which was taken directly from granitoid, while other waters at Bujanovačka Banja were taken from marl, sandstone and grus. The samples were stored in polyethylene terephthalate (PET) bottles (0.5 L) with PET caps, filled completely. pH and temperature were determined in the field, while TDS was calculated on the basis of the chemical analyses as sum of concentrations (in mg/L) of $0.6(\mathrm{Alk}) + \mathrm{Na} + \mathrm{K} + \mathrm{Ca} + \mathrm{Mg} + \mathrm{Cl} + \mathrm{SO_4} + \mathrm{SiO_2} + (\mathrm{NO_3{-}N}) + \mathrm{F}$. Chemical analyses were performed in the laboratories of the Federal Institute for Geosciences and Natural Resources (BGR) in Hannover. The bottled water labeled ID B5 (Bivoda, from the Bujanovačka Banja) was analyzed separately, in 2008, at the same laboratory (Birke et al., 2010), within the European Groundwater Geochemistry Project which resulted in the “Geochemistry of European Bottled Water” atlas (Raimann and Birke, 2010).

Table 1
Names of sampled springs and wells.

Location	Sample ID	Well ID	Sampling location	Depths of well (m)
Prolom Banja	P1	B-4	Sample taken from spa fountain (pipe from well B-4)	500
	P2	B-5	Prolom voda, bottled water	200
Ribarska Banja	R1	RB-4	Sample taken from well	852
	R2	RB-5	Sample taken from well	1543
	R3	CRB-1	Sample taken from fountain in the spa building	163
Sijarinska Banja	S1	Aragon	Sample taken from well	40
	S2	Gejzir	Sample taken from well	8.5
	S3	B-4	Sample taken from well	1232
	S4	Inhalator	Sample taken from well	9.5
Tulare	T1	BT-1	Sample taken from well	300
Viča	VC	B-1	Sample taken from well	107
Vranjska Banja	V1	Stara kaptaža	Sample taken from spring	Spring
	V2	B-1	Sample taken from spa fountain (pipe from well B-1)	120
	V3	VG-2	Sample taken from well	1064
	V4	VG-3	Sample taken from well	1470
Bujanovačka Banja	B1	Partizanska česma	Sample taken from nonthermal spring	Spring
	B2	A-2	Sample taken from well	200
	B3	A-3	Sample taken from well	162
	B4	Yu-1	Sample taken from well	210
	B5	Yu-2	Bivoda[*] bottled water	210

[*] Bottled water 0.5 L analyzed in 2008 for the European Groundwater Geochemistry Project (Raimann and Birke, 2010).

The following techniques were used for the analyses: ICP-QMS quadrupole inductively coupled plasma–mass spectrometry (Ag, Al, As, B, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Ho, I, La, Li, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sn, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb and Zr), ICP-AES inductively coupled plasma atomic emission spectroscopy (Ba, Ca, K, Mg, Mn, Na, Sr, PO_4, SiO_2), IC ion chromatography (Br, Cl, F, NO_2, NO_3, SO_4), AFS, atomic fluorescence spectrometry (Hg), titration (HCO_3), photometric methods (NH_4^+) and conductometric methods (EC). The ion balance ranged from −2.66% to 4.67%, indicating acceptable chemical analyses.

For the multivariate statistical analysis SPSS Statistics 20 for Windows was used. Q-mode cluster analysis was carried out on the original data. The samples were hierarchically clustered on the basis of all measured parameters. For Q-cluster analysis two samples (V4, B5) had to be omitted because of missing parameters (PO_4, NH_4). The distance measure used in cluster analysis was the squared Euclidean distance.

For determination of ^{222}Rn concentrations in water samples, a RAD7 instrument is used. The DURRIDGE RAD7 uses a solid-state alpha detector. A solid-state detector is a semiconductor material (usually silicon) that converts alpha radiation directly to an electrical signal (Nikolov et al., 2012). The measurement of water samples was made using the RAD7 accessory RAD-H_2O. The RAD-H_2O gives results after a 30 min analysis with a sensitivity that matches or exceeds one performed using liquid scintillation methods (Durridge Co., 2015). The activity concentrations of ^{226}Ra in the thermal water samples were also measured by the gamma-spectroscopy method (Nikolov et al., 2014).

4. Results and discussion

4.1. Chemistry of thermal water

The chemical analyses of groundwater in the SCC are presented in Table 2.

Based on the pH, the selected groundwater samples are acidic to alkaline. In the SCC region the TDS ranges from 166 to 4615 mg/L, with a median value 2411 mg/L. Groundwater from Prolom Banja and Ribarska Banja have low TDS values <1 g/L, while the water from the other analyzed sources has TDS values >1 g/L.

The TDS values have a positive Pearson correlation (Table 3) with all of the selected hydrochemical parameters, and a very strong correlation with Na ($r = 0.994$), HCO_3 ($r = 0.974$) and K ($r = 0.923$), than with Ca ($r = 0.825$), Mg ($r = 0.794$), Cl ($r = 0.8$) and B ($r = 0.713$), while very weak correlation with SiO_2 ($r = 0.167$) and F ($r = 0.099$). Temperature has a strong positive correlation with W ($r = 0.763$), Tl ($r = 0.754$), SiO_2 ($r = 0.693$), Sb ($r = 0.625$) and moderate correlation with Cu ($r = 0.58$) and Sn ($r = 0.505$). The silica in groundwater is a result of water–rock reactions. A positive correlation between temperature and SiO_2 suggests that silica geothermometers can be used to estimate aquifer temperatures. These correlations show that water temperature is related to a stage of magmatism, in which sulfides and oxides of W, Cu, Sb, Sn and Tl precipitate from hydrothermal fluids in fractures and faults. W is associated with quartz–scheelite veins which appear in a wide area around Vranjska Banja; Cu appears in porphyry orebodies (deposits at Tulare and Lece); Sb minerals appear in the Lece massif (Vukanović et al., 1972).

The strong correlation was found between temperature and Sb ($r = 0.875$) of thermal groundwater at Sijarinska Banja and Tulare. Sb usually appears in thermal waters and in deep hydrogeological structures. The maximum Sb concentrations are reached in vapor exhalations at hydrothermally active structures (not necessarily volcanic). Sb-enriched waters occur in deep fault zones and areas of young magmatism (Krainov, 2008). Hydrothermal fluids intensively kaolinized granite and schist along tension fractures in the Tupale fault zone, making them into epithermal deposits of Sb in the form of quartz–antimony veins (Vukanović et al., 1977). Magmatism in the researched area had been active during Tertiary.

With respect to cation content, the selected water samples are predominantly Na–K, while with respect to anion content, samples are mostly HCO_3 to SO_4 (Fig. 3).

Groundwater flowing through magmatic and metamorphic rocks is mainly HCO_3–Na type (Petrović et al., 2012). The lithology of the sampled locations consists of the following rock types: the most widespread is schist, followed by granitoids whose mineral composition is dominated by K, Na and SiO_2 (feldspar minerals), leading to a high content of these elements in the water. HCO_3–Na water was formed by the hydrolysis of silicate minerals with input of CO_2 at greater depth under high temperatures (Choi et al., 2005) and high pressure.

Piper's diagram (Fig. 3) shows that the water at Vranjska Banja, and Ribarska Banja and from Tulare has elevated SO_4 concentrations. Sulfur is widely distributed in reduced form as metallic sulfides (Hem, 1985). Pyrite (FeS_2) was found in a wide area around Ribarska Banja, which explains the high concentration of SO_4 in the groundwater there. Petrological analysis of cores from well V2 indicates pyritized schist and pyritized granodiorite. Tulare is characterized by hydrothermal alteration of rocks and also by the existence of Cu and Au sulfide mineralization.

The Cl–SO_4–HCO_3 ternary diagram (Fig. 4) of Giggenbach (1988) was used to classify the fresh and geothermal groundwater in the SCC region on the basis of anion concentration. As can be seen in the diagram, mature groundwater, peripheral (bicarbonate) water, volcanic and steam-heated water, as well as mixtures of all of these types, are present. Mature water is neutral thermal water with a low sulfate concentration, and a high chloride concentration, and plots along the Cl–HCO_3 axis close to the Cl^- corner (Mainza, 2006). Thermal water in the SCC region, in general, is classified as peripheral (bicarbonate) water (Fig. 4), while some samples that show an elevated sulfate concentration belong to the group of steam-heated water.

Q-cluster analysis was performed for classifying the eighteen samples on the basis of the measured 75 elements. The results of cluster analysis are shown in the dendrogram (Fig. 5) depicting the relationships among the collected samples.

The dendrogram shows two clusters: (I) from S2 to B4 ($TDS > 1$ g/L) and (II) from P1 to V3 ($TDS < 1$ g/L), and three outliers V1, T1 and VC. The main difference between the two clusters is total dissolved solids.

The groundwater samples taken from the same spa are very similar: samples from Prolom Banja (P1, P2), are very similar to each other, as well as samples from Sijarinska Banja (S1, S2, S3 and S4) and also from Ribarska Banja (R1, R3 and R2). At Bujanovacka Banja, groundwater is in direct contact with granite (B1, B2 and B3) yields very similar results, while sample B4, taken from marl and sandstone, is different from samples B1, B2 and B3.

The geology of the SCC region and deep circulation of thermal water resulted in the presence of various elements in the groundwater. The elements As, B, Ba, Be, Cs, Cu, Fe, Ga, Ge, Li, Rb, Sb, U, W, Zn and Zr are present in concentrations spanning four orders of magnitude, while only Cd, Eu, Ta and Tb are present in ranges of one order of magnitude (10^{-3} to 10^{-2}) (Fig. 6).

High concentrations of B, Ge, Rb and F were generally found in all of the analyzed samples except in those from Prolom Banja and Ribarska Banja; high F concentrations are also present in all of the samples except those from Prolom Banja. Minerals such as tourmaline, apatite, fluorite and biotite in the igneous rocks at these locations (Petrović et al., 2012) are the source of these elements in the groundwater.

Enrichment with these elements is a consequence of deep circulation of the water, residence time, and interaction between the water and the reservoir rocks. A significant number of elements appear in high concentration in the groundwater in the SCC region. A detailed description of elevated element concentrations is given in the following text.

Elevated concentrations of arsenic (As) in geothermal water are very common globally in geothermal fields. For example, concentrations of As are as high as 10,000 μg/L in the springs and geysers of Yellowstone in the USA (Stauffer and Thompson, 1984). A similar situation is recorded in geothermal water in New Zealand where As concentrations as high as 9080 μg/L have been measured (Lord et al., 2012). In sampled water from the SCC region, As concentration ranges from 0.01 to 58.6 μg/L (Table 2), with a median of 5.72 μg/L. The highest As values were determined in samples from wells B2 and B3 at Bujanovačka Banja in groundwater extracted from grus.

Elevated boron (B) concentrations were found in samples of groundwater from Sijarinska Banja, Bujanovačka Banja, and Vranjska Banja, Viča and Tulare. The average B concentration in groundwater in the SCC is 4908 μg/L, with a median of 3436 μg/L, and a maximum of 22.92 μg/L.

Boron is mostly present in tourmaline, and can be present as an accessory constituent of biotite and amphiboles (Hem, 1985). High concentrations of B were found in thermal water flowing through rocks related to volcanic and post-volcanic activity. Hydrothermal processes lead to enrichment of B, which tends to accumulate in late-stage igneous rocks, especially pegmatites (Raimann and Birke, 2010). Pegmatites are not predominant in the SCC region, so the origin of the boron in the water is unclear. Metamorphism of felsic igneous rocks found in the SCC region could be the explanation for elevated concentrations of boron and fluoride in the groundwater.

Fluoride (F) concentration is, in general, high in groundwater in the SCC (median 3.12 mg/L, maximum value 15.7 mg/L) except in the groundwater at Prolom Banja (extracted from andesites), and groundwater from wells B4 and B5 at Bujanovačka Banja (extracted from sandstone and marl). High concentrations of fluoride and carbon dioxide indicate the existence of very deep aquifers and groundwater circulation through joints and faults in metamorphic and igneous rocks (Petrović et al., 2012). The geological source of fluoride in groundwater is related to the mineral composition of fluorite, fluoroapatite, cryolite, amphibolites and micas (Dangić and Protić, 1995; Chae et al., 2007).

Groundwater from Bujanovačka Banja extracted from granite grus and granite generally has a high F concentration. Water used for bottling ("Bivoda" brand) is extracted from a shallow well in sandstone and marl in which the F concentration is low enough for this water to be suitable for drinking. Investigation of the mineral composition of grus at Bujanovačka Banja (well B2 extracts groundwater from this layer), led to discovery that mica (muscovite and biotite) as well as apatite are the main sources of F in this groundwater (Krunić et al., 2013).

Beryllium (Be) is very rare in natural water. During magmatism Be has a tendency to be accumulated in the latest phase of the igneous rocks. Be ions are small enough to replace silicon in igneous rock minerals (Hem, 1985). The highest concentration of Be in bottled water in Europe (Raimann and Birke, 2010) is found in groundwater from Portugal (64.1 μg/L) that is associated with Hercynian granite.

In the SCC region, the highest Be values (4.05 μg/L) were found in water from wells B2 and B3 (Bujanovačka Banja) extracted from grus above a Hercynian granitoid, while Be concentration is low in other wells at Bujanovačka Banja. Be concentration in thermal water at Sijarinska Banja, Tulare and Viča is greater than 1 μg/L (Fig. 6). The median Be value in thermal water from the SCC is 0.34 μg/L.

Gallium (Ga) concentration at Ribarska Banja (2.19 μg/L) is the highest of all the groundwater samples taken in the SCC. This element was found in water from well V2 at Vranjska Banja (1.27 μg/L). Significant concentration of Ga (3.88 μg/L) was found in alkaline thermal groundwater from granite, andesite and metamorphic silicate rocks in Bulgaria (Raimann and Birke, 2010), which correspond to the lithological units in the SCC region.

Elevated concentrations of germanium (Ge) were found in groundwater samples from Sijarinska Banja, Vranjska Banja and Bujanovačka Banja, as well as at Viča and Tulare locations. The highest rubidium

Table 2
Chemical analyses of thermal water of Serbian crystalline core.

		Prolom Banja		Ribarska Banja			Sijarinska Banja				Tulare	Viča	Vranjska Banja				Bujanovačka Banja				
Param	Unit	P1	P2	R1	R2	R3	S1	S2	S3	S4	T1	VC	V1	V2	V3	V4	B1	B2	B3	B4	B5
pH		8.9	9.3	9.1	9.2	8.4	6.8	6.8	6.8	6.8	6.5	7.0	7.4	7.2	8.0	8.0	6.6	6.6	6.5	6.7	6.6
EC	μS/L	212	200	417	426	424	4300	4270	4330	4320	5880	4080	1780	1400	1688	1658	2380	4260	4460	4300	4560
TDS	mg/L	166	151	299	293	300	3242	3261	3270	3271	4615	3019	1305	967	1217	1207	1803	3477	3643	3261	3666
Na	mg/L	45.3	47	88.5	88.4	82.0	1126	1126	1146	1144	1469	1135	415	285	398	386	594	1165	1257	1107	1216
K	mg/L	0.3	0.2	1.5	1.5	2.0	47.0	44.6	49.6	47.1	32.8	25.0	18.5	11.4	17.5	16.5	25	44.7	45.5	37.3	52
Ca	mg/L	5.13	1.88	1.9	2.0	8.67	35.9	39.3	33.4	39.3	141.0	19.88	13.2	19.2	8.62	11.4	51.5	94.8	61.28	65.5	85.4
Mg	mg/L	0.064	0.017	0.03	0.01	1.7	16.7	16.5	16.2	16.2	56.7	7.54	0.471	1.24	0.314	0.43	9.27	12.5	7.96	21.2	20.6
HCO_3	mg/L	124	113	111	97	149	2961	2996	2977	2969	3115	2760	559	267	488	497	1604	3070	3250	3015	3290
CO_3	mg/L	1	4	6.0	8.0	3.0	–	–	–	–	–	–	8	3	22	10	–	–	–	–	–
SO_4	mg/L	3.69	2.93	92.9	95.8	73.8	77.9	75.0	76.1	80.8	775	1.54	360	364	329	328	97.5	200	180	98.1	173
Cl	mg/L	2.48	1.79	1.78	1.78	2.64	92.0	93.3	93.1	92.4	215.0	130.0	34.6	45	48.5	47.9	22.2	56.4	54.2	52.3	54.1
I.B.	%	−2.66	0.0	1.01	2.77	1.03	0.54	0.11	1.02	1.55	2.1	2.65	3.9	1.73	4.67	3.83	1.44	1.3	0.7	1.06	0.9
Ag	μg/L	0.001	0.001	0.003	<0.001	0.001	0.007	0.005	0.004	0.003	0.013	0.004	0.003	0.001	0.001	0.388	0.004	0.004	0.004	0.006	0.003
Al	μg/L	4.3	9.8	27.1	47	2.1	2.2	2.0	2.2	5.4	12.2	6.4	125	6	13	24	9.1	16.3	3.7	12.3	1.16
As	μg/L	4.41	5.02	0.01	0.01	0.01	8.42	8.01	8.64	10.5	0.05	0.01	7.66	0.58	6.56	6.42	12.3	43.7	58.6	0.25	1.13
B	μg/L	19	24	49	51	59	7628	7386	7154	7084	18152	22925	1360	1061	1209	1190	2356	5222	4516	5054	5660
Ba	mg/L	3	2	0.003	0.005	0.007	0.303	0.353	0.371	0.337	0.019	0.26	0.061	0.052	0.054	0.073	0.016	0.043	0.095	0.104	0.152
Be	μg/L	0.002	0.001	0.034	0.034	0.026	1.39	2.03	1.28	2.24	2.54	2.96	0.652	0.367	0.319	0.255	0.117	4.05	3.3	0.025	0.013
Bi	μg/L	0.0004	<0.001	0.001	<0.001	0.001	0.007	0.001	0.002	0.001	0.005	0.002	0.002	0.001	0.002	0.002	0.001	0.002	0.002	0.001	0.002
Br	mg/L	0.012	0.011	0.006	0.006	0.010	0.146	0.241	0.201	0.145	0.563	0.228	0.049	0.066	0.072	0.071	0.052	0.099	0.121	0.131	1.71
Cd	μg/L	0.001	0.001	0.001	<0.001	<0.001	0.003	0.003	0.002	0.003	0.005	0.002	0.007	0.001	0.004	0.006	0.002	0.004	0.005	0.002	0.007
Ce	μg/L	0.001	0.001	0.011	0.005	0.001	0.004	0.004	0.003	0.01	0.035	0.011	0.082	0.006	0.004	0.012	0.07	0.047	0.012	0.133	0.003
Co	μg/L	0.003	0.004	0.005	0.004	0.003	0.006	0.003	0.004	0.015	0.005	0.006	0.13	0.004	0.006	0.008	0.028	0.048	0.009	0.051	0.026
Cr	μg/L	1.35	1.19	0.04	0.01	0.01	0.03	0.02	0.03	0.02	0.07	0.03	0.65	0.01	0.21	1.31	0.03	0.45	0.03	0.06	0.29
Cs	μg/L	0.83	1.0	4.12	3.21	4.62	101	101	102	98.7	517	40	47	35	44.4	43.7	0.25	39.3	72.6	0.24	0.385
Cu	μg/L	0.23	0.02	0.47	0.11	0.22	0.3	0.06	0.04	0.69	0.12	0.03	0.17	0.04	28	13.8	0.03	0.07	5.6	0.86	0.452
Dy	μg/L	0.001	0.001	0.006	0.002	0.001	0.002	0.006	0.003	0.004	0.056	0.108	0.034	0.018	0.002	0.003	0.037	0.05	0.04	0.019	0.003
Er	μg/L	0.001	0.001	0.004	0.001	<0.001	0.002	0.004	0.002	0.003	0.03	0.202	0.017	0.012	0.001	0.002	0.036	0.045	0.04	0.015	0.004
Eu	μg/L	<0.001	<0.001	0.001	<0.001	<0.001	<0.001	<0.001	0.001	0.001	0.007	0.001	0.011	0.002	<0.001	<0.001	0.005	0.006	0.005	0.003	0.002
Fe	mg/L	0.002	0.002	0.045	0.001	0.001	0.078	0.133	0.172	1.418	0.106	0.072	0.17	0.096	0.040	0.024	1.18	1.64	0.72	0.62	3.88
F	mg/L	0.099	0.102	2.05	2.07	1.49	3.09	3.2	3.15	3.07	4.05	15.7	11	8.88	9.3	9.17	2.68	5.81	6.78	0.7	1.16
Ga	μg/L	0.189	0.535	2.19	2.02	1.19	0.052	0.055	0.057	0.057	0.006	0.036	1.27	0.449	1.04	0.895	0.007	0.007	0.003	0.005	<0.001
Gd	μg/L	0.001	0.001	0.004	0.001	0.001	0.008	0.008	0.007	0.01	0.054	0.021	0.04	0.01	0.003	0.004	0.023	0.027	0.016	0.02	0.004
Ge	μg/L	0.27	0.35	2.78	3.19	2.87	18.9	19.2	18	19.1	36.9	141	18	16.3	17	16.7	11	31.4	34.9	8.91	16.2

Hf	µg/L	0.001	0.001	0.003	0.001	0.001	0.003	0.003	0.003	0.002	0.005	0.021	0.008	0.002	0.002	0.002	0.002	0.004	0.003	0.003	0.004
Hg	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.01	0.01	0.08	0.03	0.04	0.07	0.06	0.13	0.02	0.04	0.05	0.02	<0.01
Ho	µg/L	<0.001	<0.001	0.001	<0.001	<0.001	0.001	0.001	0.001	0.001	0.011	0.041	0.006	0.004	<0.001	0.001	0.01	0.014	0.013	0.005	0.002
I	µg/L	2.3	2.2	0.6	0.9	1	14.4	20.6	21.5	16.8	20.9	30.9	6.3	13	9.9	9.9	11	9.8	9.2	9.0	19.1
La	µg/L	0.001	0.001	0.005	0.003	<0.001	0.008	0.009	0.008	0.011	0.017	0.009	0.027	0.004	0.003	0.009	0.034	0.026	0.01	0.061	0.004
Li	mg/L	0.002	0.001	0.06	0.062	0.07	1.14	1.12	1.08	1.09	1.77	0.72	0.320	0.222	0.292	0.28	0.435	0.850	0.906	1.061	0.985
Lu	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	0.001	0.001	0.001	0.004	0.061	0.003	0.002	<0.001	0.001	0.005	0.006	0.005	0.003	0.0015
Mn	mg/L	<0.001	<0.001	0.002	0.001	0.001	0.008	0.012	0.007	0.012	0.376	0.107	0.026	0.104	0.007	0.015	0.102	0.107	0.056	0.043	0.036
Mo	µg/L	0.401	0.427	3.89	3.96	4.05	0.014	0.01	0.013	0.012	0.019	0.007	0.107	0.609	0.096	0.142	0.431	0.247	0.038	0.04	0.268
Nb	µg/L	0.002	0.001	0.001	0.002	0.001	0.003	0.003	0.003	0.002	0.003	6.37	0.004	0.002	0.002	0.002	0.003	0.003	0.002	0.004	0.006
Nd	µg/L	0.001	0.001	0.007	0.003	0.001	0.004	0.005	0.003	0.009	0.044	0.01	0.104	0.006	0.002	0.004	0.052	0.036	0.013	0.062	0.002
Ni	µg/L	0.05	0.03	0.38	0.06	0.18	0.13	0.09	0.09	0.15	0.2	0.08	0.2	0.1	0.69	0.97	0.13	0.38	0.68	0.44	1.29
Pb	µg/L	0.02	0.04	0.25	0.04	0.02	0.04	0.01	0.01	0.13	0.04	0.01	0.12	0.02	0.41	0.22	0.01	0.02	1.15	0.06	0.032
Pr	µg/L	<0.001	<0.001	0.002	0.001	<0.001	0.001	0.001	0.001	0.002	0.007	0.002	0.016	0.001	0.001	0.001	0.011	0.007	0.003	0.016	0.0005
Rb	µg/L	0.59	0.54	8.64	8.31	13.1	247	245	247	240	219	128	116	68.1	108	105	78.4	324	303	102	163
Sb	µg/L	0.103	0.32	0.008	0.003	0.011	1.49	1.58	1.58	1.74	0.008	0.003	1.02	0.136	0.947	1.18	0.004	0.035	0.14	0.027	0.813
Sc	µg/L	0.04	0.03	0.04	0.05	0.05	0.12	0.11	0.11	0.1	0.19	0.28	0.19	0.11	0.14	0.12	0.11	0.24	0.19	0.15	0.348
Se	µg/L	0.12	0.17	<0.001	0.01	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.06	0.01	0.06	0.06	0.02	0.03	0.03	0.03	0.033
Sm	µg/L	0.001	<0.001	0.003	0.001	0.001	0.005	0.006	0.005	0.007	0.023	0.009	0.035	0.006	0.002	0.003	0.017	0.015	0.009	0.018	0.002
Sn	µg/L	0.003	0.003	0.016	0.005	0.008	0.015	0.007	0.009	0.008	0.023	0.008	0.018	0.007	0.152	0.026	0.005	0.01	0.019	0.012	0.016
Sr	mg/L	0.049	0.021	0.096	0.091	0.29	1.86	1.99	1.91	1.89	**2.73**	0.515	0.666	0.663	0.674	0.634	0.895	1.69	1.56	1.19	1.49
Ta	µg/L	0.001	<0.001	0.001	0.001	<0.001	0.001	0.001	0.001	0.001	0.002	0.002	0.003	0.002	0.002	0.002	0.001	0.001	0.001	0.001	0.001
Tb	µg/L	<0.001	<0.001	0.001	<0.001	<0.001	0.001	0.001	0.001	0.001	0.009	0.008	0.006	0.002	<0.001	<0.001	0.005	0.006	0.004	0.003	<0.001
Te	µg/L	0.002	0.002	0.003	0.003	0.004	0.012	0.012	0.012	0.009	0.021	0.007	0.011	0.006	0.007	0.006	0.006	0.012	0.014	0.01	0.035
Th	µg/L	0.001	0.001	0.002	0.001	0.001	0.002	0.002	0.002	0.004	0.004	0.003	0.007	0.002	0.002	0.002	0.004	0.004	0.003	0.028	0.001
Ti	µg/L	0.21	<0.001	0.14	0.13	0.03	0.08	0.03	0.05	0.09	0.11	0.04	0.22	0.04	0.1	0.18	0.24	0.15	0.07	0.39	0.115
Tl	µg/L	0.002	0.002	0.002	0.002	0.001	0.324	0.356	0.38	0.306	0.004	0.002	0.444	0.099	0.215	0.286	0.002	0.004	0.006	0.002	0.007
Tm	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	0.001	0.001	0.001	0.004	0.044	0.002	0.002	<0.001	<0.001	0.006	0.008	0.007	0.002	0.001
U	µg/L	2.85	2.32	0.002	0.001	0.022	0.01	0.011	0.008	0.012	2.48	0.053	0.055	0.002	0.006	0.01	1.09	0.109	0.01	0.013	1.83
V	µg/L	7.78	7.95	0.01	0.01	0.01	0.08	0.15	0.06	0.12	0.32	0.07	0.11	0.01	0.01	0.04	0.05	0.31	0.05	0.06	4.45
W	µg/L	0.38	0.56	23.2	23.7	14.8	2.9	2.59	2.46	2.26	3.55	8.72	150	146	138	138	0.31	0.38	2.22	0.18	0.102
Y	µg/L	0.009	0.007	0.041	0.012	0.004	0.028	0.048	0.027	0.037	0.366	1.09	0.165	0.130	0.012	0.026	0.455	0.489	0.598	0.175	0.081
Yb	µg/L	0.001	0.001	0.002	0.001	0.001	0.004	0.004	0.002	0.004	0.025	0.375	0.017	0.015	0.002	0.002	0.036	0.048	0.041	0.016	0.009
Zn	µg/L	0.49	0.03	2.39	16.7	0.82	0.79	0.39	0.37	1.98	0.67	0.38	1.98	0.11	5.67	8.45	1.28	1.63	7.05	5.77	1.1
Zr	µg/L	0.052	0.001	0.086	0.021	0.003	0.015	0.016	0.016	0.007	0.068	2.16	0.021	0.007	0.007	0.011	0.062	0.123	0.026	0.406	1.11
NO_3	mg/L	2.31	1.59	0.006	0.01	0.012	0.02	0.01	0.01	0.02	0.02	0.01	0.06	<0.001	0.01	0.01	0.04	0.02	2.11	0.36	0.46
NO_2	mg/L	0.014	0.039	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.14
NH_4	mg/L	<0.01	<0.01	0.17	0.18	0.14	1.62	1.69	1.66	1.54	4.39	2.63	0.26	0.4	0.33	0.4	0.37	0.76	<0.01	0.01	–
PO_4	mg/L	0.09	0.05	0.03	<0.02	<0.02	0.27	0.28	0.22	0.35	0.44	0.18	0.03	0.02	0.02	–	0.14	0.38	0.3	0.8	0.65
BO_2	mg/L	0.56	0.27	1.03	0.47	0.005	29.1	28.4	28.8	28.5	73.5	91.0	5.4	4.45	5.08	5.03	8.8	18.6	16.4	19.4	
SiO_2	mg/L	32.6	27.9	43.6	43.4	38.6	66.7	65.7	66.7	67.1	52.3	28.8	117	72.7	113	110	38.6	55.7	78.1	70	88.8

Table 3
Pearson correlation coefficients between analyzed parameters of groundwater samples.

Parameters	t	pH	EC	TDS	Na	K	Ca	Mg	HCO_3	SO_4	Cl	SiO_2	F	B	Cu	Sb	Sn	Tl	W
t	1	.099	−.183	−.209	−.213	−.046	−.389	.293	−.293	.247	−.031	**.693**	.365	−.287	.580	**.625**	.505	**.754**	**.763**
pH		1	−.899	−.899	−.889	−.881	−.729	−.621	−.863	−.274	−.651	−.284	−.236	−.563	.129	−.262	.065	−.222	.165
EC			1	**.998**	**.997**	**.922**	.803	.792	**.971**	.362	.817	.173	.119	.731	−.143	.300	−.061	.173	−.373
TDS				1	**.994**	**.923**	.825	.794	**.974**	.267	.817	.167	.099	.713	−.143	.299	−.061	.173	−.373
Na					1	**.929**	.785	.762	**.983**	.206	.793	.148	.120	.731	−.152	.291	−.077	.153	−.408
K						1	.658	.585	**.943**	.061	.587	.304	.020	.477	−.098	.502	−.048	.334	−.339
Ca							1	.878	.752	.521	.662	.036	−.115	.520	−.205	−.112	−.098	−.217	−.382
Mg								1	.705	.527	.835	−.043	−.180	.659	−.239	.066	−.098	−.040	−.410
HCO_3									1	.045	.695	.061	.005	.673	−.230	.282	−.158	.107	−.527
SO_4										1	.522	.451	.307	.212	.267	−.064	.325	.082	.465
Cl											1	.0704	.302	**.882**	−.058	.241	.041	.204	−.167
SiO_2												1	.398	−.193	.594	.530	.538	.611	.703
F													1	.391	.360	.042	.315	.258	.601
B														1	−.201	.024	−.102	−.026	−.333
Cu															1	.206	**.922**	.197	.564
Sb																1	.168	**.900**	.163
Sn																	1	.173	.489
Tl																		1	.414
W																			1

(Rb) concentration was found in water from wells B2 and B3 at Bujanovačka Banja (up to 324 μg/L) and in thermal groundwater at Sijarinska Banja (247 μg/L), while higher concentrations were also measured in groundwater from Vranjska Banja and Viča and Tulare (Table 2). The median Rb concentration in the SCC region is 108 μg/L, while the median for European bottled water is 2.12 μg/L (Raimann and Birke, 2010). The largest deposits of rubidium and cesium are zoned pegmatite orebodies. Because rubidium substitutes for potassium in the crystallization of magma, the enrichment is far less effective than in the case of cesium. The source of Rb in the thermal groundwater in the SCC region may be assumed to be the igneous rocks there.

Cesium (Cs) was detected in a few of the groundwater samples from the SCC. The highest Cs concentration was measured in water from the Tulare (517 μg/L) and in water from Sijarinska Banja (100 μg/L). The

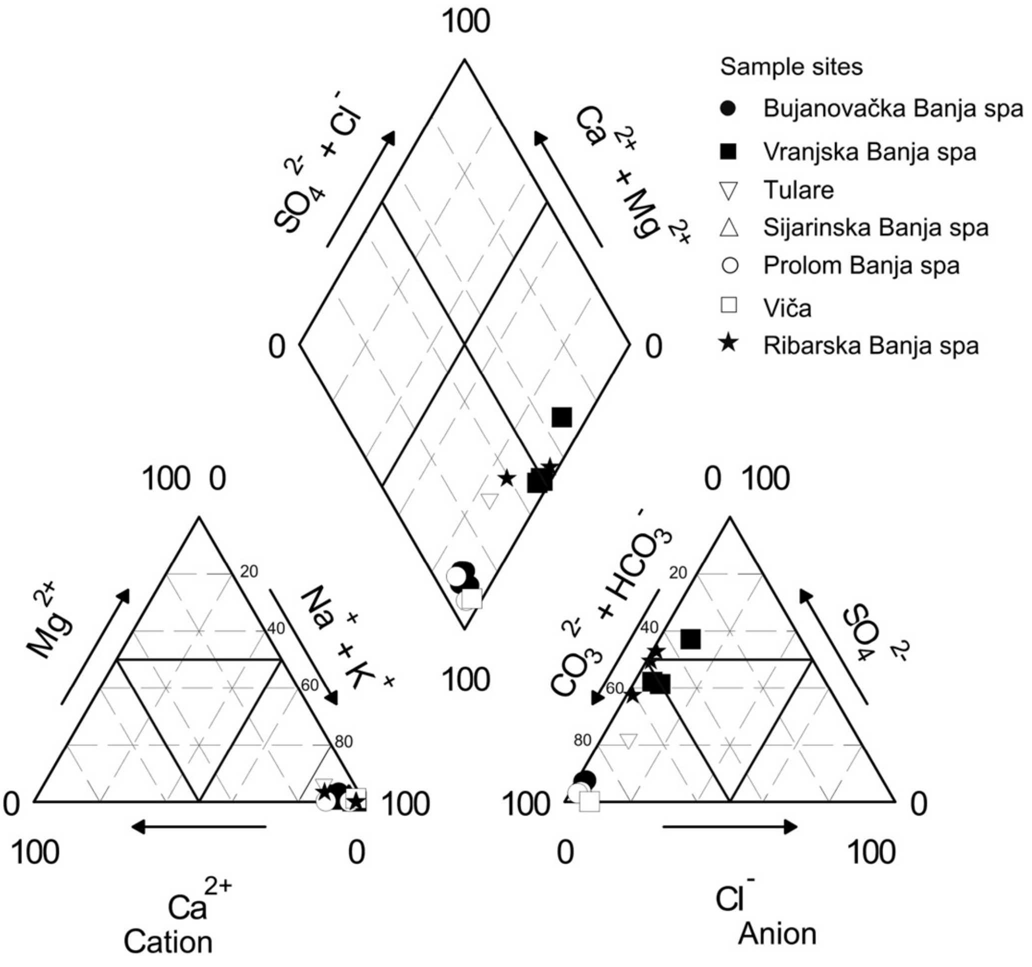

Fig. 3. Piper diagram (Piper, 1944) of thermal water in the Serbian crystalline core region.

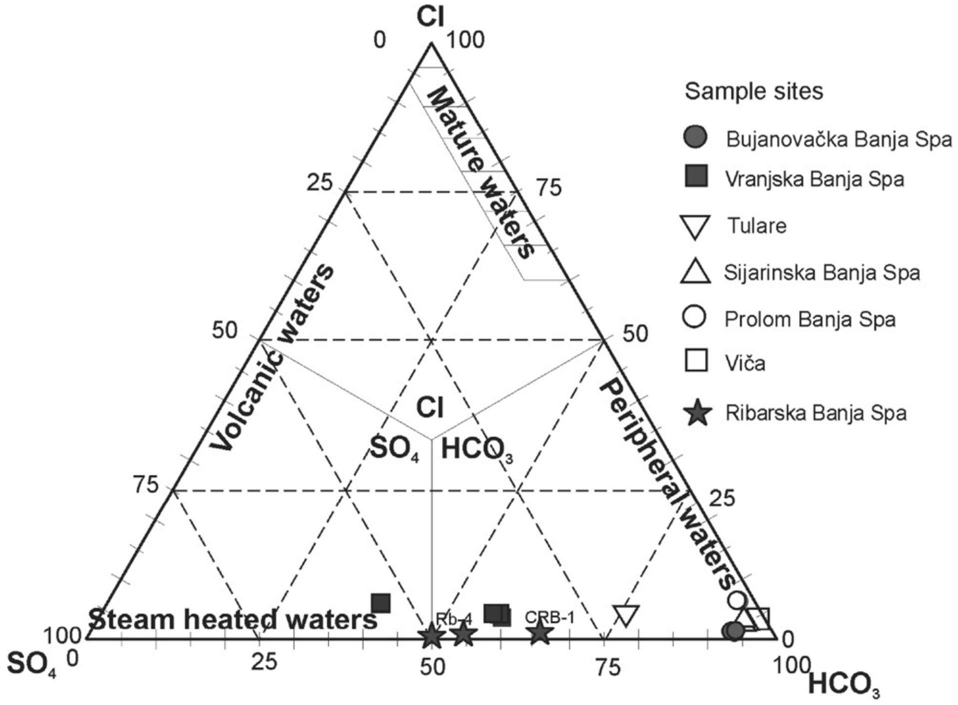

Fig. 4. Cl–SO_4–HCO_3 diagram of thermal water in the Serbian crystalline core region.

median Cs concentration in the thermal groundwater of the SCC region is 39.65 μg/L. The Cs concentration in the geothermal water is very often high.

The main sources of the Cs and Rb in the secondary minerals are the primary minerals mica and K-feldspar, where Cs and Rb can substitute for K (Raimann and Birke, 2010) due to their similar atomic radiuses. Enrichment of Cs and Rb, as well as B, F, Ge and Li in thermal water could indicate contact of the groundwater with felsic igneous rocks.

Vanadium (V) is observed in water from volcanic areas, and it is found in water in Island, the Canary Islands, Cyprus, Italy (Raimann and Birke, 2010), Argentina (Fiorentino et al., 2007), Japan (Koshimizu and Tomura, 2000), California (Wright et al., 2014) etc. The median V concentration in bottled water from volcanic rocks in Italy is 2.5 μg/L, and is lower in groundwater from metamorphic, intrusive and sedimentary rocks (Dinelli et al., 2010). A fairly high solubility of V is possible in alkaline oxidizing environments (Hem, 1985), which can explain high value of V in groundwater from Prolom Banja (pH is from 8.9 to 9.3). The main source of V in the Prolom Banja area is andesite.

High tungsten (W) concentrations were recorded in thermal groundwater from Vranjska Banja (138–510 μg/L) and from Ribarska Banja (15–24 μg/L). Most W deposits are spatially associated with granitoid where W is derived from fluids that have equilibrated with

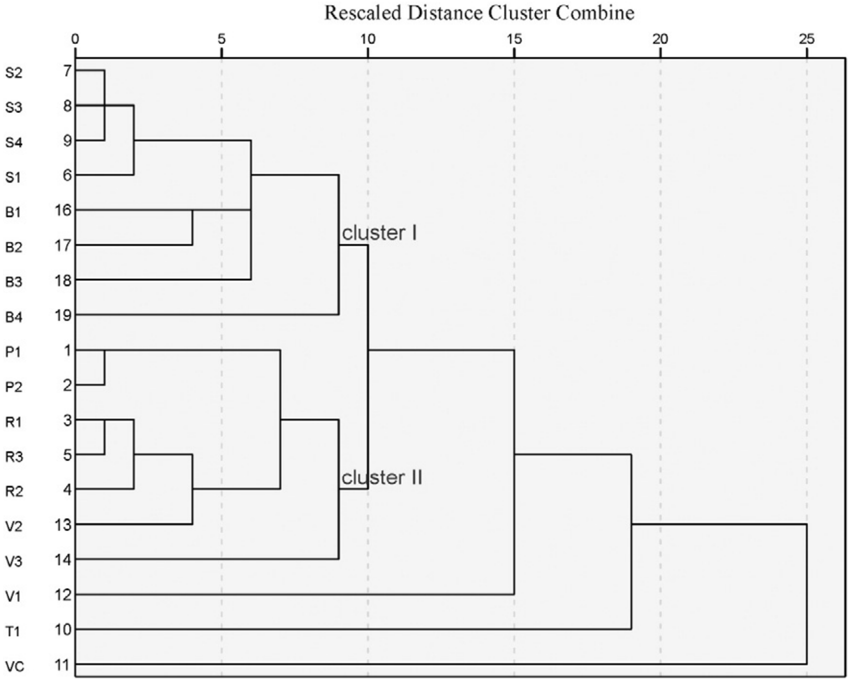

Fig. 5. Dendrogram obtained by Q-mode cluster analysis for 18 samples.

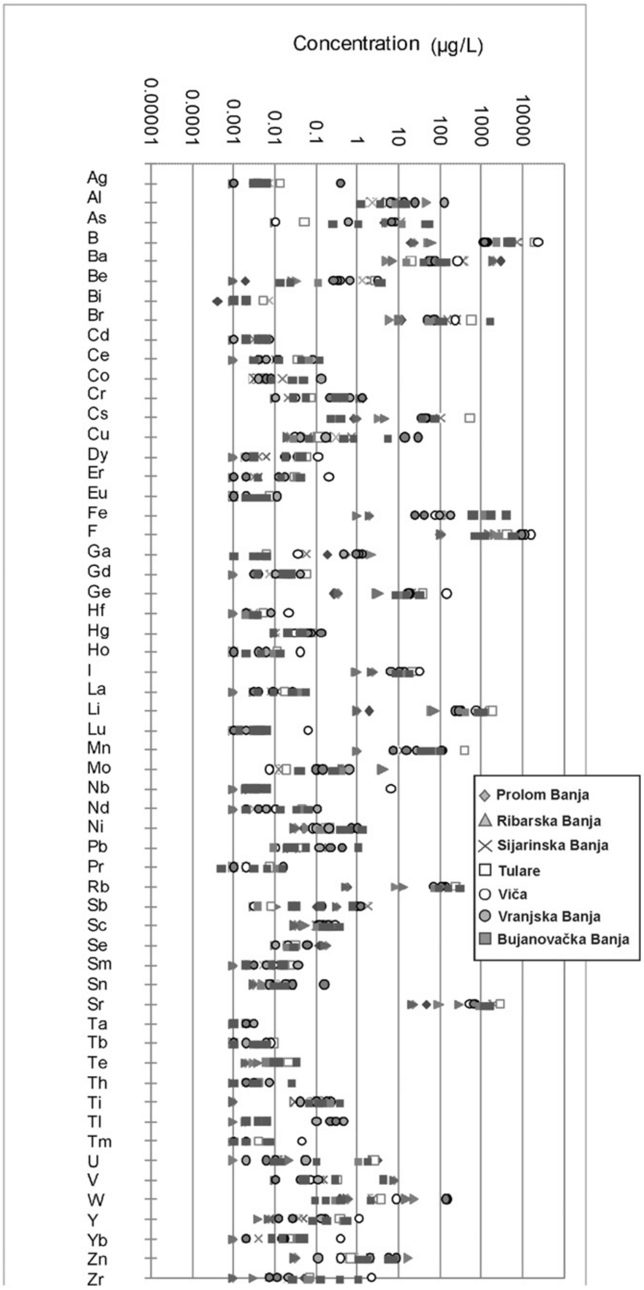

Fig. 6. Diagram of analyzed elements found in thermal groundwater in the Serbian crystalline core region (logarithmic scale).

the granitic magma and subsequently deposited in the intrusive and/or silicate and/or the carbonate country rock (Wood and Samson, 2000). Na-rich fluids may dissolve W during metasomatism and transport it as Na_2WO_4 at high temperatures (De Vos and Tarvainen, 2006). In a wide area around Vranjska Banja, quartz–scheelite veins containing high concentrations of WO_3 of 2 to 10% have been measured (Vukanović et al., 1977).

Carbonated mineral water from the well at Viča, in addition to the above-mentioned high concentrations of B, Be, Ge, Rb, W and F, also contains high concentrations of Nb and Zr, as well as rare earth elements such as Dy, Er, Ho, Lu, Tb, Tm, Y and Yb. This group of elements is known as the yttrium group or heavy rare earth elements (HREE). These elements are, as their name indicates, very rare in nature, especially in water. Their mobility is, generally, very low, so their concentrations are in the order of ng/L (Dinelli et al., 2012). All of these elements can be found in monazite, a rare earth phosphate, and xenotime, yttrium phosphate, which are found in ancient and recent placer deposits (gold, platinum, tin and diamonds), uranium ores, and weathered clay deposits, such as alkaline granites and minor intrusives, hydrothermal deposits, laterites, placers, and vein-type deposits (Hedrick, 2004). Niobium (Nb) is a trace element found in the following minerals: biotite, rutile, sphene, cassiterite and zircon. Especially geochemically important is the ionic substitution of Nb for Zr in zircon, since this mineral is widely distributed in igneous rocks (De Vos and Tarvainen, 2006). Mineralization of Nb is associated with alkaline granites and also with high concentrations of fluorine from post-magmatic alteration (Pollard, 1989). The geology in a wide area around Viča generated groundwater with a high concentration of rare earth elements, high mineralization, as well as a high content of B, F and Ge. Marbles, the presence of hydrothermal solutions, faults, igneous, metamorphic and sedimentary rocks in the near area around Viča has also influenced the chemical composition of the groundwater.

The groundwater analyses demonstrate the direct dependence between the chemical composition of the water and the geological properties of the rocks and minerals it which it flows thought faults and fractures.

4.2. Geothermometry

Chemical geothermometers (silica and cation) are used to determine the reservoir temperature of thermal water on the basis of the chemical composition of the groundwater. Silica (SiO_2) geothermometers are based on the solubility of quartz, chalcedony or amorphous silica in water, while cation geothermometers are based on the solubility of cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) in water. SiO_2 geothermometers are the most reliable for the groundwater at Bujanovačka Banja, Sijarinska Banja, Prolom Banja, Viča and Tulare, while Na–K geothermometers are reliable for water with an elevated concentration of sulfate (Fig. 3) like that at Vranjska Banja and partially at Ribarska Banja.

The temperatures calculated for the thermal groundwater at Vranjska Banja with the SiO_2 geothermometer and the Na–K geothermometer (Nieva and Nieva, 1987) were nearly the same (120–146 °C). The Na–K geothermometer (Arnórsson et al., 1983) gave the lowest temperature, or a similar temperature to the one measured at the bottom of a deep well by a temperature logger sonde (temperature of 124 °C was measured in well V4, 126 °C was measured in V4).

However, use of the Na–K geothermometers at the other groundwater occurrences in the SCC region resulted in unrealistically high values (Table 4). For water at Ribarska Banja, the Na–K geothermometer gives a higher temperature for water from well R3, which is mixed with colder shallow water (Fig. 7), than for the hottest water from wells (R1 and R2). The Na–K–Ca geothermometer could not be used due to the low content of Ca, which causes it to calculate unrealistically high temperature values.

For water at Bujanovačka Banja, a higher temperature was calculated using the Na–K geothermometer for cold water from an open granite rocks, then for other thermal water. For groundwater from Prolom Banja, very low temperature was calculated with the Na–K geothermometer (Arnórsson et al., 1983) (Table 4). This groundwater is extracted from andesite and, therefore, the best choice is the use of chalcedony geothermometers.

Based on SiO_2 geothermometers (Table 4) the lowest expected reservoir temperature is at Prolom Banja (45–54 °C, water temperature measured at the wellhead: 30 °C) and the highest expected is at Vranjska Banja (118–146 °C, water temperature measured at the wellhead: 80–105 °C). The expected temperature of the reservoir at Ribarska Banja is 90–97 °C (water temperature measured at the wellhead: 38–54 °C), at Sijarinska Banja 115 °C (water temperature measured at the wellhead: 77 °C), at Bujanovačka Banja 90–123 °C (water temperature measured at the wellhead: 20–46 °C), at Tulare 104 °C (water temperature measured at the wellhead: 26 °C) and at Viča 79 °C (water temperature measured at the wellhead: 24 °C).

Table 4
Temperatures of thermal groundwater in the Serbian crystalline core region calculated using SiO_2 and Na-geothermometers.

Location	Well	Tm^1 (°C)	T^2_q (°C)	T^3_q (°C)	T^4_q (°C)	T^5_q (°C)	T^6_{ch} (°C)	T^7_{ch} (°C)	T^8_{Na-K} (°C)	T^9_{Na-K} (°C)	T^{10}_{Na-K} (°C)	T^{11}_{Na-K} (°C)	$T^{12}_{Na-K-Ca}$ (°C)	T^{13}_{K-Mg} (°C)
Prolom Banja	P1	33	82.8	86.1	83.4	83.8	54.2	51.7	80.6	49.7	59.2	21.0	176.6	45.2
	P2	32	76.4	80.4	76.9	77.4	47.8	44.9	64.1	33.5	42.6	4.2	191.8	50.4
Ribarska Banja	R1	41.5	90.1	92.4	90.6	91.0	61.4	59.4	121.6	90.3	100.8	64.4	365.7	90.5
	R2	54.0	95.5	97.1	95.9	96.2	66.8	65.1	121.7	90.4	100.9	64.5	361.9	105.4
	R3	38.7	95.3	96.9	95.8	96.0	66.6	64.9	140.2	108.9	119.9	84.9	294.0	50.4
Sijarinska Banja	S1	66.0	115.7	114.5	115.9	115.0	87.2	86.95	171.0	140.2	152.0	120.1	779.3	98.1
	S2	68.0	115.0	113.9	115.2	114.3	86.4	86.13	167.8	137.0	148.6	116.4	747.4	96.8
	S3	76.0	115.7	114.5	115.9	115.0	87.2	86.95	173.2	142.5	154.3	122.7	811.8	100.0
	S4	54.7	116.0	114.8	116.2	115.3	87.5	87.28	170.1	139.4	151.1	119.1	764.1	98.6
Tulare	T1	27.2	103.9	104.4	104.2	104.1	75.3	74.15	135.5	104.3	115.1	79.7	519.2	73.5
Viča	VC1	23.6	77.7	81.6	78.2	78.7	49.1	46.29	134.8	103.5	114.4	78.9	715.0	91.9
Vranjska Banja	V1	81	146.1	140.2	145.8	141.7	118.1	120.5	176.6	146.0	157.9	124.9	629.5	122.7
	V2	77	120.1	118.2	120.2	118.9	91.6	91.7	165.9	135.0	146.7	117.1	476.2	95.0
	V3	105	144.1	138.5	143.9	140.0	116.1	118.2	176.3	145.6	157.5	123.9	678.1	127.3
	V3	103	142.6	137.2	142.3	138.6	114.5	116.5	175.7	145.1	156.9	121.8	620.8	120.6
Bujanovačka Banja	B1	13	90.1	92.4	90.6	91.0	61.4	59.4	176.1	145.5	157.3	120.7	535.7	89.2
	B2	46	123.8	121.4	123.9	122.2	95.4	95.7	171.3	140.5	152.3	114.1	610.9	100.7
	B3	20	106.9	106.9	107.2	106.9	78.3	77.4	174.7	144.1	155.9	110.1	685.6	107.5
	B4	29	118.2	116.6	118.3	117.2	89.6	89.6	168.4	137.6	149.3	105.3	621.1	98.0
	B5	29	130.6	127.2	130.6	128.3	102.3	103.2	172.6	141.9	153.7	121.9	662.2	88.8

1) Measured temperature on the surface.
2) SiO_2 geothermometer — Fournier, 1977.
3) SiO_2 geothermometer — Fournier, 1977.
4) SiO_2 geothermometer — Fournier and Potter, 1982.
5) SiO_2 geothermometer — Fournier and Potter, 1982.
6) SiO_2 geothermometer — Arnórsson et al., 1983.
7) SiO_2 geothermometer — Fournier, 1977.
8) Na–K geothermometer — Giggenbach, 1988.
9) Na–K geothermometer — Nieva and Nieva, 1987.
10) Na–K geothermometer — Fournier, 1979.
11) Na–K geothermometer — Arnórsson et al., 1983 (t = 25–300 °C).
12) Na–K–Ca geothermometer — Fournier and Truesdell, 1973.
13) K–Mg — Giggenbach, 1988.

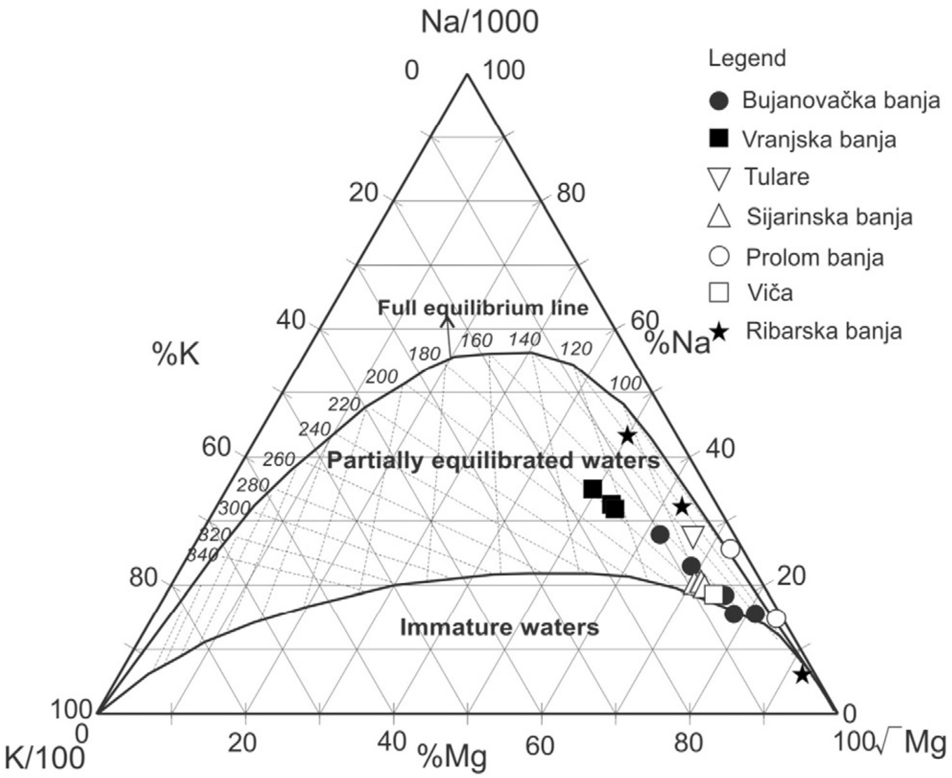

Fig. 7. Na–K–$Mg^{0.5}$ triangular diagram of thermal groundwater in the Serbian crystalline core region.

Contents of Mg are lower in the groundwater at these locations, so K–Mg geothermometers are not recommended.

Giggenbach (1988) has proposed a graph from which the expected temperatures can be determined on the basis of Na/K and K/Mg$^{0.5}$ geothermometers and it can also give the "maturity" of the thermal water. In the Na–K–Mg diagram (Fig. 7), it can be seen that most of the water occurrences in the SCC region are in the zone of partial equilibrium with the host rocks. That means the groundwater that has reached equilibrium with the minerals (geothermal water) is mixed with groundwater that has not reached the equilibrium (nonthermal groundwater). Thus, groundwater which plots near the corner of the $\sqrt{\text{Mg}}$ value (Fig. 7), near the boundary of "immature" water, has an elevated proportion of nonthermal groundwater. The groundwater presented in the $\sqrt{\text{Mg}}$ value corner of the diagram is from a cold spring at Bujanovačka Banja, and from the coldest well (R3) at Ribarska Banja. Only groundwater from Prolom Banja reaches full equilibrium with the host rocks, or the groundwater is in equilibrium with andesites.

4.3. ^{222}Rn and ^{226}Ra in the thermal groundwater in the Serbian crystalline core

From the hydrogeological aspect, the presence of ^{222}Rn in the water was evaluated for its use in estimating groundwater flow. The concentration of ^{222}Rn in groundwater is primarily controlled by the concentration of U and Th in the rocks, as well as the emanation coefficient of radon (Garver and Baskaran, 2004). The emanation coefficient of radon is fraction of the total amount of radon produced by radium decay that escapes from the soil particles and gets into the pores of the medium (Todorović et al., 2015). The emanation coefficient of radon is high when the groundwater flows through tectonic zones (Przylibski, 2000; Przylibski, 2011) and weathering zones (Przylibski and Zebrowski, 1999; Przylibski, 2000). ^{222}Rn concentration in a groundwater is directly controlled by the lithology of the aquifer (Michel, 1991). Water enriched with Rn usually is highly mineralized or has a high temperature or elevated CO_2 concentration compared to the groundwater in the surrounding area (Protić, 1995). Concentrations of ^{222}Rn and ^{226}Ra were determined in 14 samples of thermal water collected in the SCC region (Todorović et al., 2012; Nikolov et al., 2014). ^{222}Rn concentrations in the water are quite high except for sample B4 from Bujanovačka Banja and P2 from Prolom Banja (Table 5). Water from well B4 is the only sample extracted from marl and sandstone, while water from well P2 is from andesite. It can be seen that ^{222}Rn concentration is higher in water which flows through crystalline rocks and granites. High concentrations of radon are commonly found in water from fracture zones in crystalline rock (Leonard and Janzer, 1978), so ^{222}Rn anomalies have been used to locate faults (Gerardo et al., 2000). High radon concentrations are observed in the water in nearby tectonic zones, where the fractures and faults are the most common path for the ^{222}Rn migration to the surface (Todorović et al., 2015). Water from shallow well R3 in Ribarska Banja has the highest concentration of ^{222}Rn, and this water is from a fault zone in schist, while groundwater from deep wells (R1 and R2), has a lower ^{222}Rn concentration, and higher ^{226}Ra concentration. This happens when upwelling anoxic thermal groundwater is mixed with cold, oxygen rich water leading to iron hydroxide precipitation scavenging ^{226}Ra from the thermal water and thus forming an efficient radon source (Surbeck, 2005; Todorović et al., 2015). Also, this area is marked with neotectonic movement, so a high concentration of ^{222}Rn could indicate an active fault zone.

High ^{222}Rn concentration in water does not always indicate the presence of ^{226}Ra (Onishchenko et al., 2010). Concentrations of ^{226}Ra are low in all of the water samples, confirming that concentrations of ^{222}Rn are not proportional to the concentrations of ^{226}Ra in the analyzed samples (Fig. 8).

Table 5
Activity concentration of ^{222}Rn and ^{226}Ra in the thermal groundwater in the Serbian crystalline core region (Nikolov et al., 2014).

Location	Well	Activity concentration of ^{222}Rn (Bq L^{-1})	Activity concentration of ^{226}Ra (Bq L^{-1})
Prolom Banja	P2[*]	14.3 ± 3.5	
Ribarska Banja	R1	42 ± 7	0.32 ± 0.19
	R2	54 ± 8	0.48 ± 0.18
	R3	104 ± 15	0.26 ± 0.08
Sijarinska Banja	S1	52 ± 9	0.41 ± 0.18
	S2	48 ± 6	0.45 ± 0.09
	S3	32 ± 7	0.37 ± 0.08
Tulare	T1	52 ± 10	0.35 ± 0.18
Vranjska Banja	V1	26 ± 4	0.35 ± 0.16
	V2	48 ± 5	0.27 ± 0.07
Bujanovačka Banja	B1	46 ± 9	0.21 ± 0.09
	B2	30 ± 11	0.47 ± 0.20
	B3	52 ± 13	0.32 ± 0.17
	B4	10.4 ± 0.9	0.48 ± 0.09

[*] Source Todorović et al., 2012.

5. Conclusions

Thermal groundwater is present at seven locations within the hydrogeological region of the SCC. Water is extracted from Tertiary andesite (Prolom Banja), grus, marl and sandstone (Bujanovačka Banja) and mostly from crystalline rocks (Ribarska Banja, Sijarinska Banja, Vranjska Banja, Viča, Tulare). The maximum measured temperature of thermal groundwater in the SCC is 105 °C.

All of the water samples are of HCO_3–Na to SO_4–Na type. Groundwater in the SCC region ranges from acidic to alkaline, sometimes it is low mineralized and sometimes highly mineralized.

At Prolom Banja, the groundwater has a high V concentration indicating its origin from andesites. According to the trace elements, this thermal water is completely different than other analyzed groundwaters. In all other waters F concentration is high, which indicates dissolved granitoid minerals, apatite, biotite, fluorite, as well as groundwater circulation through joints and faults in metamorphic and igneous rocks. High concentrations of B, Be, Ge and Rb are found in groundwater at Sijarinska Banja, Tulare, Viča and Bujanovačka Banja originated from felsic igneous rocks, although the water is directly extracted from other rock types (schist, gneiss, granite grus, sandstone and marl). Cs concentration is also high in water at Sijarinska Banja and Tulare. A relationship to grus was found in two samples from Bujanovačka Banja. W in groundwater at Vranjska Banja is related to quartz–scheelite veins which contain a high concentration of WO_3. Groundwater at Viča has the highest trace element concentrations. Beside the aforementioned elements, this groundwater also contains Zr, Nd and HREE.

Based on SiO_2 geothermometer measurements in the SCC region, it has been determined that the expected reservoir temperature at Vranjska Banja is up to 146 °C, which is the highest expected temperature in this region. The maximum expected temperature of groundwater

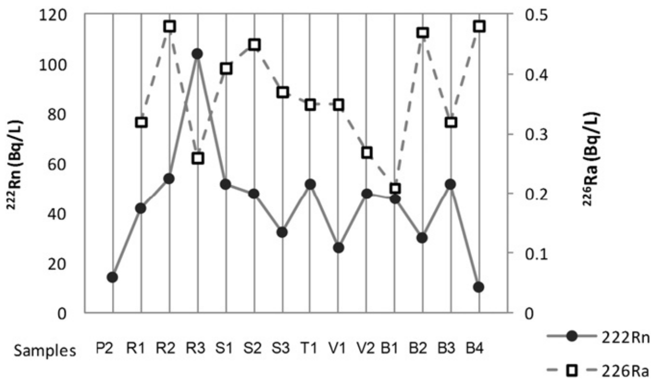

Fig. 8. ^{222}Rn and ^{226}Ra concentrations in thermal groundwater in the Serbian crystalline core region.

at Sijarinska Banja is 115 °C, at Bujanovačka Banja 90–123 °C, and at Ribarska Banja up to 97 °C, while at Prolom Banja it cannot be more than 55 °C. Cation geothermometers are not reliable or do not show acceptable temperatures for the selected groundwater samples.

According to the Na–K–$Mg^{0.5}$ diagram, immature water is present in cold spring and thermal groundwater, which is mixed with cold surface water. Full equilibrium with the host rock reaches only groundwater from andesite rocks, while other groundwater from schist, granites and granodiorites is in partial equilibration with the host rock.

^{222}Rn in groundwater is shown to be useful for identification of faults and fractures, especially identification of active fault zones. It can also be seen that ^{222}Rn concentration is higher in water which flows through crystalline rocks and granites than in marls, sandstone and andesites.

The geology of the SCC has resulted in thermal water with a wide range of temperatures and chemical compositions thus, various applications of these groundwater occurrences are possible.

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