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Rare earth elements in some bottled waters of Serbia

MAJA TODOROVIĆ¹, PETAR PAPIĆ¹, MARINA ĆUK¹ & JANA STOJKOVIĆ¹

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

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

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

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

Introduction

The mostly trivalent rare earth elements (REE) consist of group IIIb transition elements Sc, Y and La and inner transition elements (or lanthanides). In geo-

chemistry the term 'rare earth elements' generally refers only to the lanthanides (La–Lu). Yttrium (Y) behaves similarly to the lanthanides Dy–Ho and thus is commonly included in discussions of the REE. Scandium (Sc) in contrast, is substantially smaller cation

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

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

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

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

which they flow, although they can show different REE patterns compared with their aquifer rock.

Understanding the geochemistry of REE in circum-neutral pH terrestrial waters, such as groundwaters, is important from both the standpoint of their potential use for investigating water–rock interactions, as well as for tracing groundwater flow (MCCARTHY *et al.* 1998; JOHANNESON *et al.* 2000). Moreover, ascertaining the behavior of the REE in natural terrestrial waters is especially significant in the study of the fate and transport of radioactive transuranics in the environment because of the chemical similarities of the REE and trivalent transuranics i.e., Pu³⁺, Am³⁺, Cm³⁺, and Cf³⁺; (CHOPPIN 1983; KRAUSKOPF 1986; MCCARTHY *et al.* 1998). Therefore, it is generally well accepted that the ubiquitous and naturally occurring REE can be used as chemical analogs for studying the behavior of the highly radioactive transuranics in natural waters.

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

Some of their unique composition features, such as elevated carbon dioxide (CO₂), hydrogen sulphide (H₂S), sulphate (SO₄²⁻), iron and high salt content are specific to the geological and hydrogeological position of the exploited springs and producing wells. However, these naturally occurring waters are often chemically processed before bottling in order to adjust to market needs. The final bottled water product can have, therefore, little resemblance to the original groundwater composition. Nevertheless, MISUND *et al.* (1999), found a traceable link between bottled water composition and aquifer lithology in 66 European bottled waters. GROSELJ *et al.* (2008) used neural networks to arrive at the same conclusion. REIMANN & BIRKE (2010) analyzed 1785 bottled waters and they believed that those analysis may provide a possibility to gain an idea about groundwater chemistry at the European scale. According to this study, from the aspect of rare earths, for the most elements in the group, there is no unambiguous geological explanation for high occurrences in groundwater. In general, the highest concentration of rare earth elements, from lithological aspect, are related to pegmatite dyke containing REE minerals, felsic gneisses, granite and calcalkaline Tertiary volcanics (REIMANN & BIRKE 2010).

Methods

During the spring and summer of 2012, 21 bottle waters available on the Serbian market were pur-

chased in selected shops all over Serbia. The dominant role for selection bottled water sources played their different genesis and discharge. Different conditions of water formation reflect their variations in chemical types.

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

Results and Discussion

Geological setting of rare earth elements

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

Rare earth deposits in igneous rocks can be grouped into five distinct categories differing in the provenance and evolution of the magma and in the rock types hosting mineralization: (1) carbonatites, (2) peralkaline silica undersaturated rocks, (3) peral-

kaline granites and pegmatites, (4) pegmatites associated with sub- to metaluminous granites, and (5) Fe oxide-phosphate.

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

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

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

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

Major hydrochemistry and hydrogeochemistry of rare earth elements

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

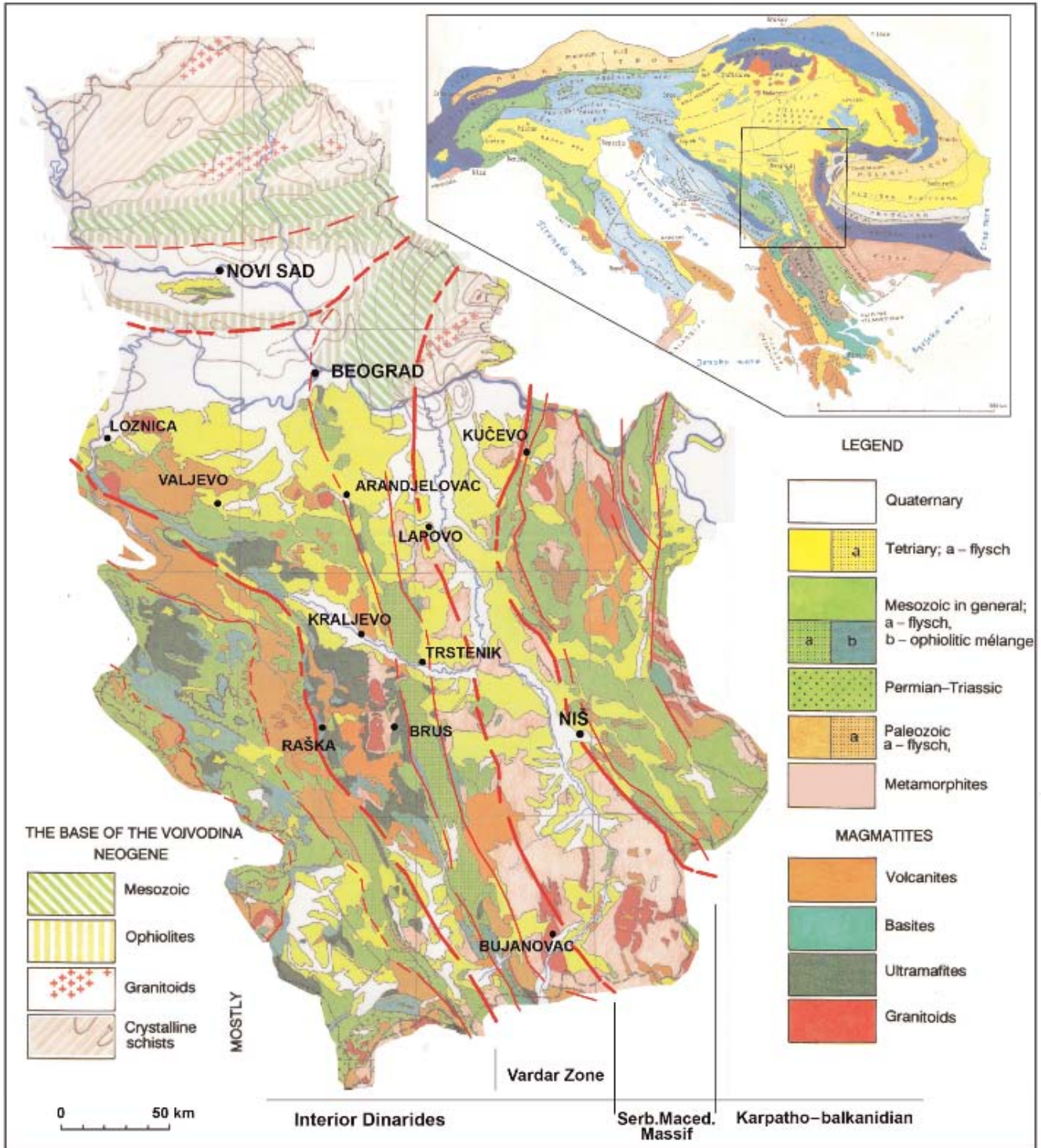


Fig. 1. Geological map of Serbia (DIMITRIJEVIĆ 1994).

Durov diagram, showing the anions, cations, TDS and pH levels in parallel (Fig. 2). The trilinear diagram of the anions shows minor differences in anionic composition; most of the bottled water samples were of the hydrocarbonate type, with only Brand 2 being of the $\text{HCO}_3\text{-Cl}$ type and Brand 14 of the $\text{HCO}_3\text{-SO}_4$ type.

With regard to cationic compositions, there were two large groups: one dominated by calcium and magnesium – 7 samples $\text{HCO}_3\text{-Ca}$, 2 samples $\text{HCO}_3\text{-Mg}$ (TDS up to 804 mg/L), and the other by Na – 12 samples $\text{HCO}_3\text{-Na}$ (TDS up to 3100 mg/L). No significant correlation between the macrocomponents was

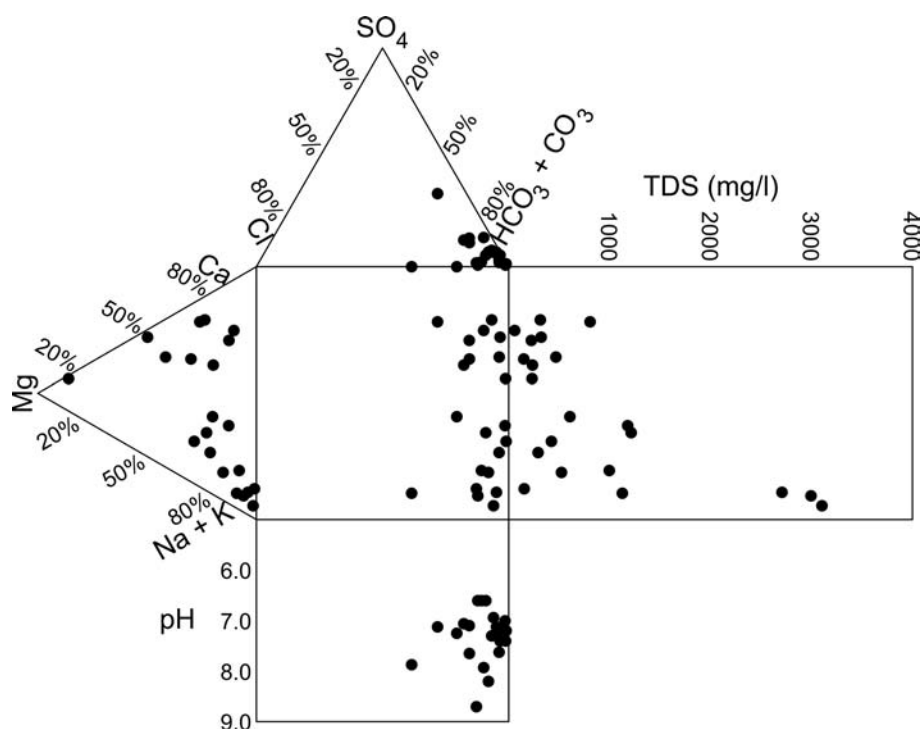


Fig. 2. Durov diagram of chemical compositions of bottled water samples.

noted, except between sodium and hydrocarbonates. Among the bottled water samples of the Na-HCO₃ type, 8 brands exhibited a TDS level greater than 1000 mg/L, of which 7 featured natural carbon dioxide (Brands 5, 7, 10, 15, 16, 17 and 18).

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

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

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

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

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

REE totals are shown in Fig. 4a. Brands 8, 9 and 20 exhibited the lowest summary REE concentrations,

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

REE in concentrations from 23.04 to 86.6 ng/L were found in bottled water samples of different cation types and TDS levels (from Ca-HCO₃ to Na-HCO₃, Na-HCO₃-Cl, TDS 146–1123 mg/L). This group included waters tracing to limestones (Brands 19 and 21), marls (Brand 12), gneissic granites (Brand 4), and inter-

granular porosity rocks of different compositions (Brands 2, 3, 6 and 13).

Levels above 100 ng/L were recorded in bottled water samples whose chemical compositions were directly or indirectly affected by granitic intrusions and Tertiary magmatism. Similar to the previous samples, TDS did not correlate with total REE. This group included naturally carbonated waters (Brands 5, 7, 10, 15, 16, 17 and 18, Na-HCO₃, TDS 994–3100 mg/L),

Brand 14 (Ca-HCO₃-SO₄, TDS 804 mg/L), and Brands 1 and 11 (TDS 221 and 420 mg/L). Figs 4b and 4c show total light lanthanides and heavy lanthanides (with yttrium), by sample.

Light lanthanides measured from 3.6 to 1449.63 ng/L. Cerium (Ce) and lanthanum (La) were the greatest contributors to these concentrations. The highest LREE concentrations were recorded in all naturally carbonated water samples (except Brand 10), as well as in Brands 1 and 14, where apart from lithology, the solubility capacity of CO₂ has a considerable effect. HREE concentrations ranged from 0 to 136.19 ng/L. Higher HREE concentrations were measured in samples

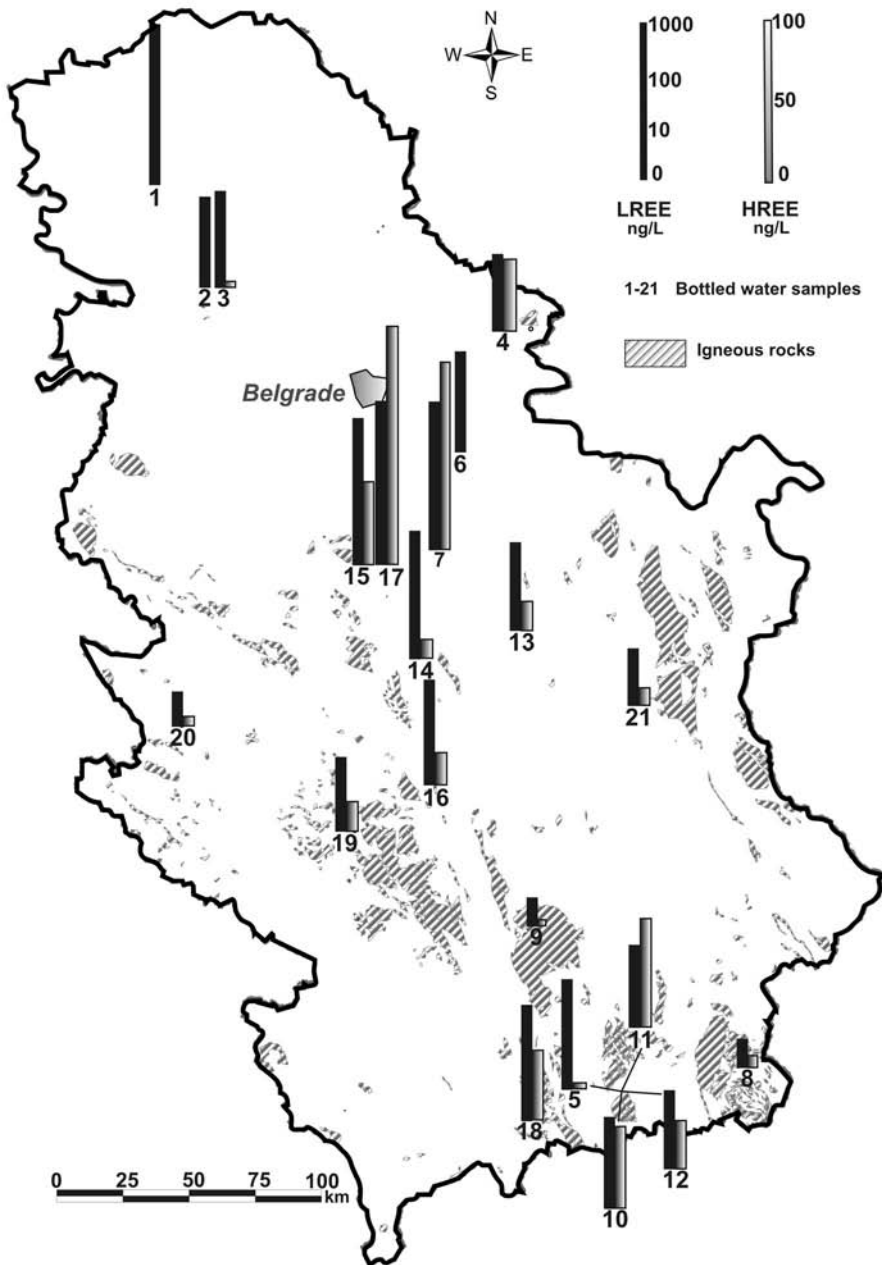


Fig. 3. Schematic map of Serbia with concentrations of LREE and HREE in analyzed bottled waters and distribution of igneous rocks.

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

Although Brands 19 and 21 represented groundwaters tracing to limestones with low total REE, there were notable differences between both the REE totals and in terms of a higher HREE concentration in Brand

19. Additionally, the elevated temperature and the presence of heavy lanthanides in the groundwater used to bottle Brand 19 suggested a potential influence of groundwater from granitoid and metamorphic rocks on the recharge of the aquifer formed in limestones from which this water is tapped.

REE concentrations in groundwater generally depend on several factors: release into solution during the dissolution of minerals, pH levels and redox states of the groundwater, adsorption, complexing ligands in the groundwater and hydrogeological factors (e.g. flow pathways and residence time). The environmental behavior of the REE and yttrium is strongly influenced by solution chemistry (WOOD 1990; LUO & BYRNE 2004). In groundwater, REE are subjected to chemical complexation with several potential REE complexing agents. Trivalent REE are considered to be hard ions and will complex preferentially with hard ligands including F^- , SO_4^{2-} , CO_3^{2-} , PO_4^{3-} and OH^- . In general, simple ions (Ln^{3+} , Ln is any lanthanide) and sulfate complexes are dominant at low pH levels, while at circumneutral to basic pH, REE frequently occur as carbonate and dicarbonate ions (BROOKINS 1989; WOOD 1990; JOHANNESSON *et al.* 1996). In addition, fluoride and phosphate complexes may

be important where ligand concentrations are high (WOOD 1990; SHAND *et al.* 2005). The REE display strong sorption characteristics, particularly at high pH, onto mineral surfaces which reduces REE abundance in solution.

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

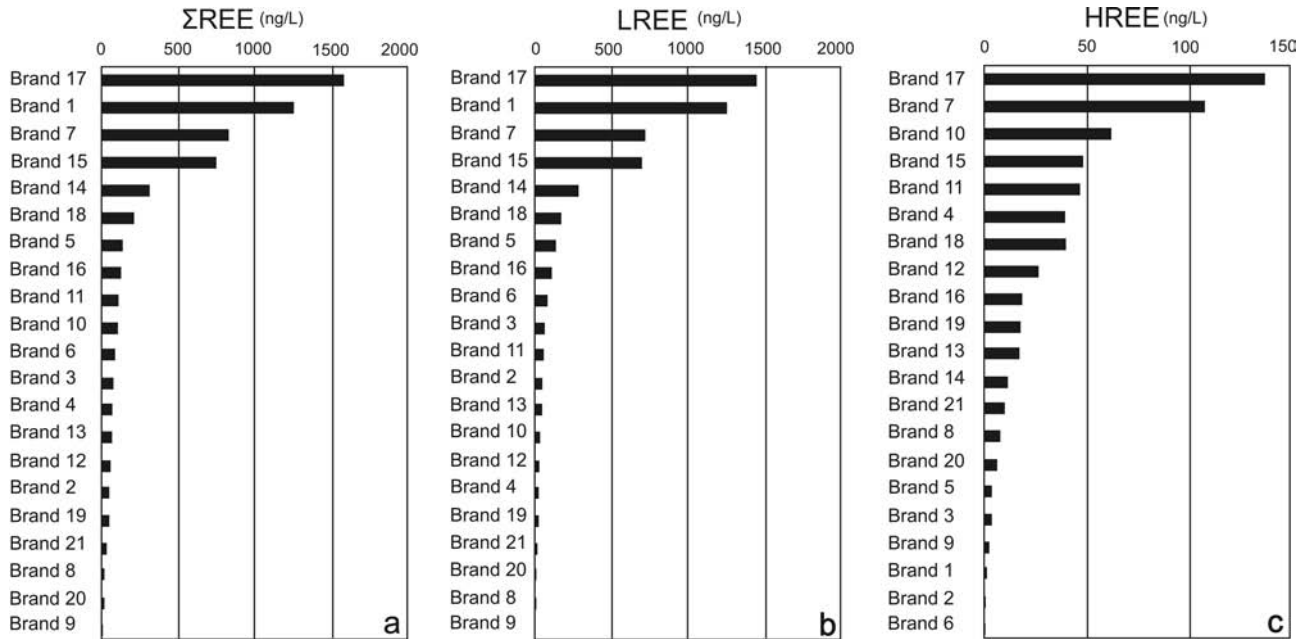


Fig. 4. Total REE (a), LREE (b) and HREE (c) in bottled water samples.

tled water samples, the pH levels in that range characterized naturally carbonated waters, where REE complexation is generally dominated by the formation of carbonate complexes, LnCO_3^+ and $\text{Ln}(\text{CO}_3)_2^-$.

HREE occurrences in the bottled water samples were associated with the formation of carbonate complexes, particularly the dicarbonate ion (i.e., $\text{Ln}(\text{CO}_3)_2^-$), whose stability in groundwater increases with increasing atomic number. In relation to LREE, this contributes to greater stability of the HREE in alkaline groundwaters. Where aquifers are devoid of heavy lanthanide-carrying minerals, only light lanthanides are found. If lithological conditions for the occurrence of HREE in groundwater exist, they will dominate the LREE, particularly at high pH levels, because of both the stability of their dicarbonate forms and the removal of LREE from the groundwater as they are generally scavenged through sorption processes much more than the HREE.

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

It should be noted that the bottled water was technologically treated in some cases and this may have lead to reduced REE concentrations. For example, CO_2 degassing increases pH and leads to carbonate precipitation. Due to cooling, silica, sulphides, and/or various oxihydroxides flocculate, and many trace ele-

ments are sorbed or co-precipitated. Furthermore, change of pressure and temperature during ascent of water induces formation of metastable components and surface coatings, and ion exchange as a function of fluid flow (MÖLLER 2002).

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

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

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

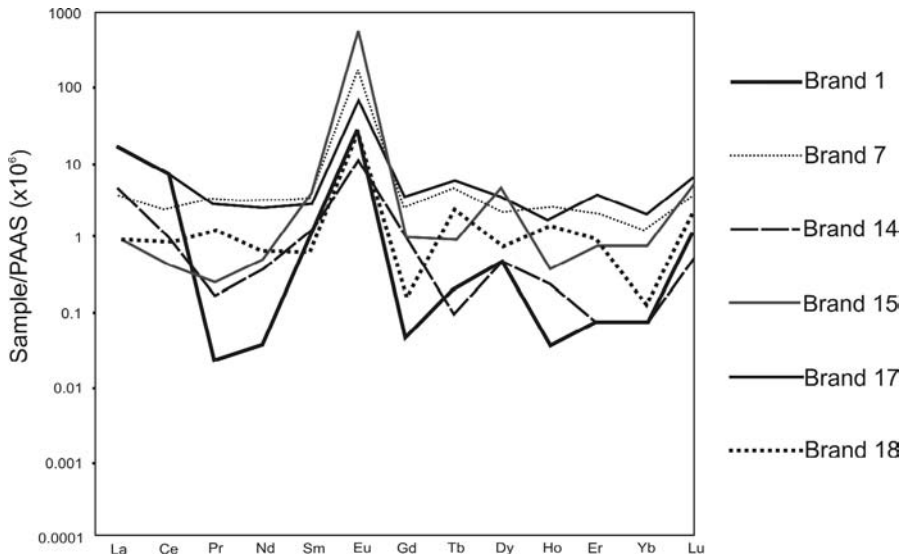


Fig. 5. REE patterns (normalized to PAAS) of bottled water samples.

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

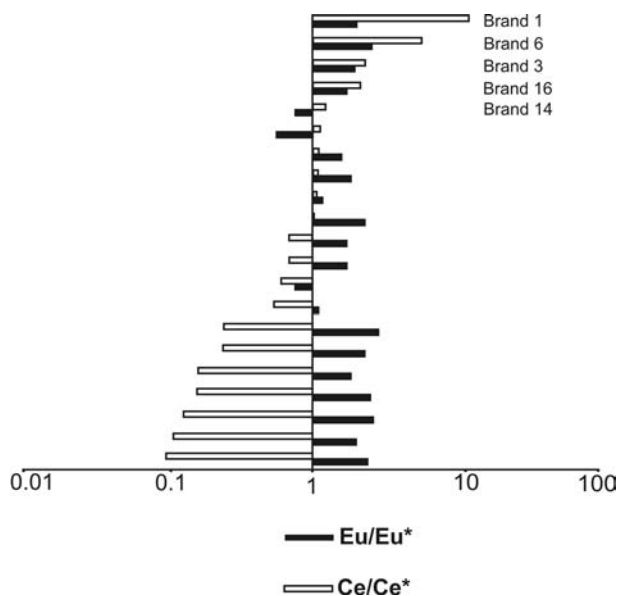


Fig. 6. Ce and Eu anomalies in bottled water samples.

Among the studied samples, a great positive Ce anomaly was noted in four cases. The anomaly is only slightly negative for the high TDS Na- HCO_3 water

type and especially prominent for the Ca-Mg- HCO_3 water type. The negative Ce anomaly may be a result of redox transformations of Ce^{3+} into Ce^{4+} , as anoxic groundwater discharges to the Earth's surface (LEYBOURNE & JOHANNESSON 2008), due to cerianite (CeO_2) precipitation or adsorption to Fe oxyhydroxides (BAU 1999; DIA *et al.* 2000). Experimental data (BAU 1999) indicate that adsorption of Ce onto iron oxyhydroxides is a relatively slow process so the variations in the magnitude of the Ce anomaly could result in the difference in residence time of circulation groundwater. Negative Ce anomalies are quite

common in oxygen rich waters. For instance, seawater, oxygen-rich river and karst waters are characterised world-wide by negative Ce anomalies (MÖLLER 2002).

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

Conclusion

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

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

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Резиме

Елементи ретких земаља у неким флашираним водама Србије

Елементи ретких земаља (ЕРЗ) анализирани су у 21 узорку флашираних вода са територије Срби-

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

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

Резултати досадашњих истраживања на територији Србије са аспекта проспекције ЕРЗ, указују да су главни минерали носиоци ЕРЗ монацит, ксенотим, аланит, апатит, бетафит, фергусонит, цир-

кон, колумбит, који су углавном констатовани у гранитоидним стенама и метаморфним стенама непосредног омотача гранита и у наносима потока и река који протичу кроз гранитоидне масиве Цера, Вршца, Букуље, Чемерног, Жељина, Бујановца, Голије итд. Највеће концентрације ЕРЗ и тешких лантанида у флашираним водама се налазе управо у областима ових масива, што се може повезати и са појавом угљен–диоксида у околини Букуље и Бујановца, чија растварачка способност доприноси бржем ослобађању ових елемената из стена. Значајан параметар који утиче на ЕРЗ,

посебно лаке лантаниде (La, Ce и Eu) је оксидо–редукциони потенцијал. У већини узорака установљена је негативна аномалија церијума, док скоро сви узорци имају позитивну аномалију еуропијума. Негативна аномалија церијума последица је брзог уклањања Се из воде и указује на нагле измене оксидо–редукционог потенцијала подземних вода, док позитивна аномалија еуропијума указује на редукциону средину унутар које циркулишу воде, растварање плагиокласа обогаћених Eu или специфичним условима који омогућавају већу миграцију двовалентног еуропијума.