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Trace and Rare Earth Element Geochemistry of Croatian Thermal Waters

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ABSTRACT: Concentrations of 42 trace elements, including rare earths, in Croatian thermal waters were investigated. Originating from different parts of Croatia, i.e. different types of aquifers, studied thermal waters provide insight into the range of concentrations of broad spectrum of elements in Croatian thermal waters. Covering a wide range of temperature (30 - 92 °C), studied thermal waters are generally classified as geothermal springs (Hrvatsko Zagorje and Lipik) and low-temperature geothermal reservoirs (Bizovac), differing from each other not only by temperature but also by geochemical composition. Thermal waters from Bizovac Spa, from the eastern part of Croatia, were found significantly enriched in majority of measured elements in comparison with waters from Hrvatsko zagorje and Lipik. Significant variability between studied waters was also observed regarding the rare earth elements levels and fractionation patterns, substantially different normalized REE patterns and wide range of Eu and Ce anomalies, ranging from 0.10 to 0.84 and from 3.48 to 159, respectively. Characterized by near-neutral to alkaline pH (6.8 - 8.1) and great variability with respect to the geochemical composition, studied waters were found to primarily reflect the underlying geology.

Key words: Thermal water, Geochemistry, Trace elements, Rare earth elements, Croatia

INTRODUCTION

Mineral and geothermal waters differ from other groundwater according to the amount of dissolved minerals and the temperature. Their chemical composition depends on the specifics of the environment in which they were generated and water–rock interaction processes along the way from the source to the surface. For this very reason studies on distribution of trace elements, including rare earth elements, in geothermal waters increases our understanding of the conditions under which these elements can be mobilized, contributing in the field of geochemistry as well as petrology. Extensive literature is available which deals with the connection of geochemical composition of groundwater and host rock of the aquifer (Banks *et al.*, 1999; Johannesson *et al.*, 2000; Janssen and Verwiej 2003; Lee *et al*. 2003; Kharitonov *et al*. 2007; Leybourne and Johannesson 2008, Guo *et al*. 2010 and reference therein) and will not be discussed here in details. Croatia is a country rich in hot springs and has a long tradition of exploiting geothermal resources with most significant geothermal potential from resources in the eastern part of Croatia. So far the geothermal waters were exploited mainly for medicinal and recreational purposes. Available literature on geochemistry of Croatian thermal waters includes studies on natural radioactivity of thermal waters with regard to radium (Bituh *et al.*, 2009) and radon (Radolić *et al.*, 2005) activities, exposure to radioactivity (Marović and Senčar, 2001) from natural thermal waters and associated health risks (Marović *et al.*, 1996). The literature on the subject of the multielement composition of Croatian thermal waters is almost nonexistent, and the available information is scarce (Miholić, 1940; Miholić, 1945; Miholić 1959). The objectives of this study are thus as follows: 1) to assess the levels of trace and rare earth elements in thermal waters originating from different regions in Croatia; 2) to get an overview of spatial variations in REE abundances and fractionation patterns; 3) to determine the major processes and factors controlling the concentrations of these elements in thermal waters.

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MATERIALS & METHODS

On the territory of Croatia there are two distinct regions that differ in values of geothermal gradient and heat flux density, as well as in geological aspect: the Dinarides area with a very small number of occurrences of thermal water and the Pannonian basin with a much larger number of occurrences of geothermal water different in chemical composition and temperature. Dinarides occupy the south-western part of the country with predominantly Mesozoic carbonate rocks characterized by the geothermal gradients ranging from 0.01 to 0.03 °C/m (terrestrial heat-flow density: 20 - 60 mW/m^2). The north-eastern and eastern part of the country lies mostly in the Pannonian basin. It is dominated by sedimentary rocks of Quaternary and Tertiary age that overly the crystalline bedrock and, occasionally, the Mesozoic sedimentary rocks. The gradient of this area is moderate to high and ranges from 0.03 to 0.07 °C/m (more than the world mean value) with considerable geothermal energy potential. The terrestrial heat-flow density is also high, ranging from 60 to 100 mW/m^2 and occasionally up to 120 mW/m^2. The present-day high heat flow in the Pannonian basin can be explained by depth dependent extension of the lithosphere, which occurred during Early to Middle Miocene time (Royden *et al.*, 1983; Royden and Dövényi, 1988; Lankreijer *et al.*, 1995; Sachsenhofer *et al.*, 1997, Lenkey *et al.*, 2002).

The geothermal areas and locations in Croatia where geothermal waters were studied (Fig. 1) are as follows: (i) Geothermal area of Hrvatsko zagorje (T=32-58°C) – Stubica Spa, Krapina Spa, Tuhelj Spa, (ii) Geothermal area of Međimurje – Podravina (T = 58 °C) – Varaždin Spa; (iii) Geothermal area of West Slavonia (T = 25 – 60 °C) – Lipik Spa; (iv) Geothermal area of East Slavonia (T = 74 – 125 °C) – Bizovac Spa (springs: Bizovka and Slavonka). Hrvatsko zagorje and Međimurje – Podravina area is located in the north-eastern part of Croatia and encompasses a border zone between Alps, Dinarides and Pannonian basin. This area is influenced by many tectonic movements that belong to the final stages of the Variscan orogeny and the entire Alpine orogenetic cycle. The most important role in the formation of spas in this area was played by tectonic movements during the Miocene, Pliocene and Quaternary. Thermal waters of Hrvatsko zagorje (including Krapina Spa, Stubica Spa, Tuhelj Spa and Varaždin Spa in a broader sense) are considered to be of vadose origin, largely accumulating in Triassic limestones and dolomites. Triassic carbonates as conductors and collectors of rainwater are open to sufficiently large areas so that they can accumulate sufficient rainfall water and supply multiple thermal springs. Apart from thermal sources, Triassic carbonates supply numerous sources of drinking water, which further emphasizes the need for knowledge on water composition, ensuring their future protection and sound management.

The Lipik Spa and Bizovac Spa are located in eastern part of Croatia, south-western part of Pannonian basin. With regard to the classification of geothermal resources, a wider area of Hrvatsko zagorje and Lipik can be described as areas of geothermal springs with water temperatures below 65 °C, while only the area of Bizovac belongs to low-temperature (65 – 100 °C) geothermal reservoirs. In the latter the

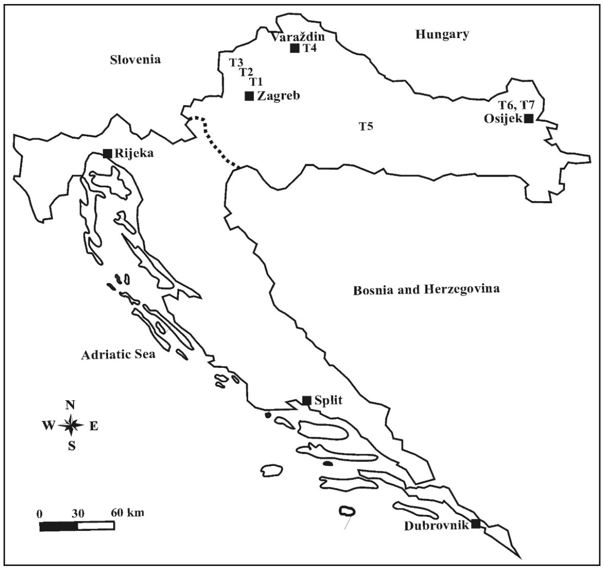

Fig. 1. Map of sampling locations (---- boundary between regions of different geothermal gradient and heat flux density, Dinarides in west and Pannonian basin in east).

water is pumped from deep aquifers (with depths up to 5000 m), composed of heterogeneous mixed layers of permeable (sands and sandstone) and impermeable (clay and shale) deposits with permeable sediments saturated with brine water.

Samples of thermal waters were collected in 2012 directly from the springs from the north-eastern and eastern parts of Croatia, and brought to the laboratory immediately after collection. Sample locations of the analyzed thermal waters are shown in Fig. 1. The associated sample IDs are also given in Table 1. Upon arrival to the laboratory all water samples were filtered through a 0.45 µm filter paper, stored in plastic containers and acidified with concentrated HNO_3 to pH 2 to minimize precipitation and adsorption onto container walls.

Mulitielemental analysis of the prepared samples was performed by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICPMS) using an Element 2 instrument (Thermo, Bremen, Germany). More details on the used analytical method are described earlier (Fiket *et al.* 2007).

The measurements of the selected isotopes were performed at three different resolutions: low resolution (^{7}Li, ^{9}Be, ^{85}Rb,^{95}Mo, ^{109}Ag, ^{111}Cd, ^{120}Sn, ^{121}Sb, ^{133}Cs, ^{205}Tl, ^{208}Pb, ^{209}Bi, ^{238}U), medium resolution (^{23}Na, ^{25}Mg, ^{27}Al, ^{42}Ca, ^{47}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe,^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn,^{86}Sr, ^{89}Y, ^{138}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{145}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{171}Yb, ^{175}Lu) and high resolution (^{75}As, ^{77}Se).

External calibration was used for the quantification. Standards for multielemental analysis were prepared by appropriate dilution of a multielemental reference standard (Analytika, Prague, Czech Republic) containing Al, As, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sr, Tl, V and Zn in which single element standard solutions of U (Aldrich, Milwaukee, WI, USA), Sn (Analytika, Prague, Czech Republic) and Sb (Analytika, Prague, Czech Republic) were added. A multielemental reference standard (Analytika, Prague, Czech Republic) containing Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y and Yb was used for rare earth elements determination. Prior to analysis samples were acidified with 2 % (v/v) HNO_3 s.p. and In (1 µg/L) as internal standard was added. No additional dilution of samples was performed and all samples were prepared in triplicate.

Water samples were analyzed for total concentration of 42 elements (Ag, Al, As, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Gd, Ho, La, Li, Lu, Mn, Mo, Nd, Ni, Pb, Pr, Rb, Sb, Se, Sm, Sn, Sr, Tb, Ti, Tl, Tm, U, V, Y, Yb and Zn). Selection of isotopes of the elements to be determined was made for the isotopes free from isobaric interferences, except for the monoisotopic elements. Limits of detection were calculated as three times the standard deviation (3σ) of the blank values. Quality control of analytical procedure used for multielemental analysis was performed by simultaneous analysis of the blank and certified reference material for water (SLRS-4, NRC, Canada). Good agreement between the analyzed and certified concentrations within their analytical uncertainties for all elements was obtained.

RESULTS & DISCUSSION

The pH values of sampled waters ranged from neutral (6.8 – 7.2) to alkaline (7.6 – 8.1), whereas water temperature ranged from 30 °C to 92 °C (Table 1). The obtained temperatures are consisted with the results of previous studies (Marović *et al.*, 1996; Bituh *et al.*, 2009). The results of measurement of 42 elements (Ag, Al, As, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Gd, Ho, La, Li, Lu, Mn, Mo, Nd, Ni, Pb, Pr, Rb, Sb, Se, Sm, Sn, Sr, Tb, Ti, Tl, Tm, U, V, Y, Yb and Zn) in thermal water samples are shown in Table 2 and Table 3. To describe the entire group of REE, for purpose of statistical analysis, the sum of all element concentrations (ΣREE) as the key parameter was used.

Investigated waters show considerable variability in the element composition with some of the elements varying up to four orders of magnitude (Sb, Se and Tl; Table 3). Antimony and thallium were found to range from bellow the detection limits to 47.4 µg/L and 3.79 µg/L, respectively, whereas selenium was present at concentrations from 0.002 µg/L to 29.0 µg/L. Litophile elements (Sr, Ba and Li) were found dominant in studied waters. Their concentrations cover wide range of values from 314 µg/L to 78 mg/L for Sr, from 98 µg/L to 52 mg/L for Ba and from 8.05 µg/L to 2.8 mg/L for Li. Significant variability was also observed for Be, Cs and Rb, with concentrations ranging from below detection limits to 0.778 µg/L, from 0.254 µg/L to 95.4 µg/L, and from 3.91 µg/L to 308 µg/L, respectively. Lithium was found to be positively to highly positively correlated with Be and Rb (c.c. from 0.77 to 0.97, Table 3). These elements (Li, Rb, Be and Cs) are typical geogenic elements and their presence in thermal water is considered to reflect the geochemical characteristics of local aquifers, especially its clay content, i.e. aluminosilicate component of the aquifer.

Rubidium and cesium are elements which exhibit similar chemical behavior and readilly substitute for potassium in minerals. Cesium has the ability to preferentially adsorb on clay minerals compared to rubidium, while rubidium, due to its smaller ionic radius, would more readily incorporate into clay minerals substituting for potassium (Brouwer *et al.*, 1983; Berger

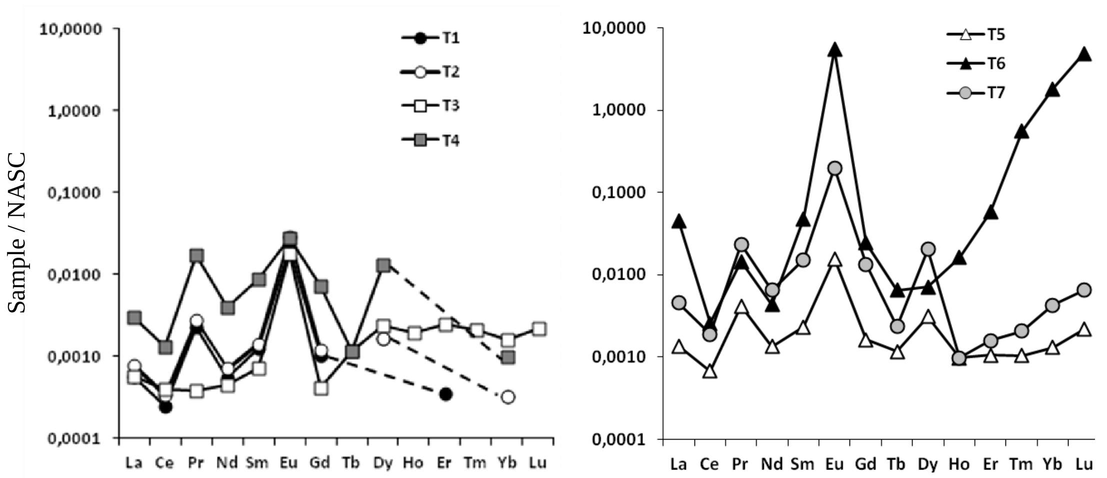

Fig. 2. NASC-normalized REE patterns for thermal water samples.

Table 1. Temperature, pH and other characteristics of thermal and mineral spring waters in Croatia.

Water sample	Description*	Temperature (°C)	pH
Stubica Spa (1)	Optimal mineral composition	51.8	6.9
Tuhelj Spa (2)	Mineral water	30.1	8.1
Krapina Spa (3)	Thermal water rich in Ca, Mg and HCO_3^-	39.2	7.2
Varaždin Spa (4)	Thermal water abundant with sulfur	54.6	6.8
Lipik Spa (5)	Thermomineral water rich in F, Na, Ca and HCO_3^-	~ 60	7.2
Bizovac Spa (spring: Bizovka) (6)	Hypothermal salt water rich in minerals	92	7.9
Bizovac Spa (spring: Slavonka) (7)	Thermal salt water rich in minerals	81	7.6

* (Marović *et al.*, 1996)

et al., 1988; Viellard, 2000). The Rb/Cs ratio in the water can therefore be modified by alteration of feldspars and biotite and subsequent clay mineral formation and consequently be used as tracer of water–rock interaction and alteration processes (Hart, 1969; Aquilina *et al.*, 1997; Göb *et al.*, 2013). Average Rb/Cs ratios of the crust range from 25 to 30 (Taylor and McLennan, 1985), whereas McDonough *et al.* (1992) found that a variety of sediments and sedimentary rocks (including loess) have an Rb/Cs ratio of 19 (± 11, 1σ). In this study Rb/Cs ratios cover relatively broad range of values, from 2.1 to 16.8. Percolating of water through clay-rich sedimentary rocks, Cs sorbs onto the clays and Rb/Cs ratios in the waters increase. High Rb/Cs ratios are thus considered a characteristic of waters originating from or passing through clay-rich sedimentary rocks, in this case thermal waters from Tuhelj Spa (T2) (Rb/Cs = 15.4) and Krapina Spa (T3) (Rb/Cs = 16.8). The lowest Rb/Cs ratio was observed for thermal water from Bizovac Spa (spring Bizovka, T6) (Rb/Cs = 2.1), which suggest that water from this location is in equilibrium with the alteration mineral assemblage (illite and kaolinite or chlorite) of the surrounding rock.

Compared with the values reported for spring and mineral water from the territory of Croatia (Fiket *et al.*, 2007) measured concentrations in thermal waters covered by this study were found comparable for majority of elements. The exception is thermal water from Bizovac Spa (T6 and T7) in which much higher concentrations of As, Cd, Sb, Se, Sr and Tl were measured. The obtained element concentrations were further compared with the maximum contaminant level (MCL) regulated by Croatian (NN, 2008), WHO (2011) and EPA (2003) directives for ground, drinking and tap water (Table 1). In thermal water from Bizovac Spa (spring Bizovka, T6) several elements (As, Ba, Fe, Mn and Sb) were found at levels exceeding Croatian legislation and EPA regulations. Selenium was found at concentrations above Croatian and WHO directives, although bellow MCL set by EPA regulations. Antimony level in this sample was found to exceed the WHO guidelines as well. At spring Slavonka (T7) measured concentrations of As, Fe and Mn were also found at levels exceeding Croatian legislation and EPA regulations. In general, thermal water from Bizovka (T6) contains higher concentrations of all measured elements compared with water from other locations.

Table 2. Basic descriptive statistical parameters for the distribution of trace and rare earth elements in thermal water samples (mean – average value, min – minimum, max – maximum, STD – standard deviation) expressed in µg/L.

	Mean	Min	Max	STD		Mean	Min	Max	STD
Ag	0.013	0.002	0.035	0.015	**Sr**	11757	314	77842	29143
Al	9.45	2.65	24.0	8.19	**Ti**	0.204	0.068	0.470	0.151
As	84.9	0.116	550	205	**Tl**	0.634	<0.001	3.79	1.40
Ba	7632	98	52114	19616	**U**	0.089	0.019	0.275	0.088
Be	0.251	0.001	0.778	0.350	**V**	0.136	0.008	0.725	0.262
Bi	0.001	<0.001	0.004	0.001	**Zn**	17.9	5.49	29.8	9.37
Cd	0.163	0.004	1.05	0.393	**Y**	0.001	<0.001	0.004	0.001
Co	0.071	0.006	0.303	0.106	**La**	0.209	0.018	1.41	0.454
Cr	0.410	0.132	1.17	0.359	**Ce**	0.078	0.017	0.172	0.063
Cs	19.6	0.254	95.4	34.4	**Pr**	0.058	0.003	0.181	0.065
Cu	3.39	0.418	8.70	3.20	**Nd**	0.066	0.013	0.177	0.058
Fe	237	4.46	1161	416	**Sm**	0.051	0.004	0.268	0.086
Li	627	8.05	2754	1046	**Eu**	0.765	0.019	6.41	2.12
Mn	30.9	1.13	102	37.0	**Gd**	0.028	0.002	0.120	0.040
Mo	1.31	0.041	4.25	1.55	**Tb**	0.002	<0.001	0.006	0.002
Ni	0.452	0.075	0.975	0.309	**Dy**	0.025	0.007	0.086	0.027
Pb	0.567	0.175	2.13	0.698	**Ho**	0.003	<0.001	0.017	0.005
Rb	84.9	3.91	308	120	**Er**	0.021	<0.001	0.164	0.054
Sb	7.17	<0.001	47.4	17.8	**Tm**	0.030	<0.001	0.267	0.089
Se	4.21	0.002	29.0	10.9	**Yb**	0.620	0.001	5.54	1.85
Sn	0.073	0.009	0.384	0.137	**Lu**	0.248	<0.001	2.23	0.742

Concentration of elements in this geothermal water are elevated from a few (Al, Be, Cr, Mn, Mo, Ni, Pb, Rb and Zn) to as much as 400 times (Se) in comparison to average value from all other locations.

The elements (As, Ba, Cd, Co, Cs, Fe, Li, Mn, Mo, Pb, Sb, Se, Sn, ΣREE, Ti, Tl and Y) were found positively to highly positively correlated with the correlation coefficients (c.c.) ranging between 0.77 and 1.00 (Table 3). Their relationship probably derives from their highest concentration measured in thermal water from Bizovac Spa (T6). In the area of the eastern Croatia, elevated As and Fe concentrations in groundwater were explained by their natural enrichment in the surrounding rocks of the aquifer (Ćavar *et al.*, 2005; Ujević *et al.*, 2010; Romić *et al.*, 2011), while Li, Cs and Ti are typical geogenic elements and major constituents of various silicate minerals. Their high positive correlation with the abovementioned elements (Ba, Cd, Co, Mn, Mo, Pb, Sb, Se, Sn, ΣREE, Tl and Y) corroborates their common, natural, source.

Uranium and vanadium were found highly positively correlated with each other (c.c. = 0.84, Table 3). These elements were found at highest levels in thermal water from Stubica Spa (T1) in which the highest concentration of zinc was also measured. Additionally, in this thermal water sample higher concentrations of lead and copper were also recorded compared with concentrations measured in the other thermal waters from Hrvatsko zagorje and Lipik (T2 – T5). Conducted geological studies in Hrvatsko zagorje indicate that increased content of lead, zinc or silver can be linked to local geology and the Middle Triassic volcanism (Strmić Palinkaš *et al.* 2013).

Concentrations of the REEs in analyzed thermal waters range over three orders of magnitude, from less than 0.001 µg/L to 6.41 µg/L. Of all the measured REE Eu and Yb were found at highest concentrations, whereas concentrations of Tb, Ho, Er, Tm and Lu were either very low or below the detection limit of 0.001 µg/L at some locations. Analyzed thermal waters displayed variations in terms of REE concentrations as well as distribution patterns, with ΣREE ranging from 0.114 µg/L in thermal water from Stubica Spa (T1) to 16.9 µg/L in thermal water from Bizovac Spa (spring Bizovka, T6).

All thermal waters have negative Ce anomaly ($Ce/Ce^* = Ce_{NASC}/(La_{NASC} \times Pr_{NASC})^{0.5} = 0.10 – 0.84$) and positive Eu anomaly ($Eu/Eu^* = Eu_{NASC}/(Sm_{NASC} \times Gd_{NASC})^{0.5} = 3.48 – 159$). Similar findings were recorded for groundwaters from this area (unpublished data). The prevailing negative Ce anomalies are considered to be caused by oxidative removal processes involving Ce (Janssen and Verweij 2003), reflecting the generally oxic conditions of sampled waters. In oxidazing groundwater Ce can precipitate as

Table 3. Mean concentrations of elements (μg/L) obtained for thermal water (T1-T7) samples (n = 3).

	T1	T2	T3	T4	T5	T6	T7
Ag	0.003	0.002	0.033	0.004	0.010	0.035	0.005
Al	2.80	4.14	5.47	2.65	10.1	17.0	24.0
As	7.30	0.179	0.116	0.567	7.59	550	28.2
Ba	114	164	97.8	163	105	52114	662
Be	0.009	0.001	0.181	0.002	0.778	0.733	0.054
Bi	<0.001	0.002	<0.001	0.001	<0.001	0.002	0.004
Cd	0.024	0.007	0.004	0.004	0.009	1.05	0.037
Co	0.013	0.052	0.006	0.014	0.021	0.303	0.085
Cr	0.262	0.250	0.132	1.17	0.331	0.525	0.197
Cs	1.97	0.254	6.46	0.260	24.2	95.4	8.8
Cu	4.40	0.855	1.70	1.21	0.418	8.70	6.47
Fe	6.11	8.75	79.7	4.46	198	1161	205
Li	31.3	8.05	170	9.63	1300	2754	114
Mn	2.18	1.22	53.7	1.13	31.9	102	24.4
Mo	0.915	0.432	0.041	0.561	0.363	4.25	2.64
Ni	0.663	0.570	0.256	0.075	0.209	0.975	0.416
Pb	0.381	0.175	0.239	0.204	0.313	2.13	0.530
Rb	12.9	3.91	33.2	4.35	308	198	34.4
Sb	0.394	0.006	0.005	<0.001	1.64	47.4	0.768
Se	0.095	0.008	0.035	0.002	0.379	29.0	0.009
Sn	0.019	0.009	0.021	0.010	0.038	0.384	0.030
Sr	752	314	931	317	1089	77842	1053
Ti	0.118	0.088	0.338	0.068	0.114	0.470	0.234
Tl	0.084	0.001	0.004	<0.001	0.380	3.79	0.176
U	1.00	0.221	0.070	0.101	0.306	0.348	0.119
V	0.275	0.074	0.019	0.033	0.083	0.102	0.033
Y	0.017	0.014	0.107	0.008	0.046	0.725	0.038
Zn	29.8	8.22	28.1	14.0	5.49	22.2	17.3
Rb/Cs	6.5	15.4	5.1	16.8	12.7	2.1	3.9
La	0.018	0.024	0.018	0.095	0.043	1.41	0.142
Ce	0.017	0.023	0.027	0.087	0.045	0.172	0.127
Pr	0.018	0.022	0.003	0.132	0.032	0.112	0.181
Nd	0.015	0.020	0.013	0.111	0.037	0.118	0.177
Sm	0.007	0.008	0.004	0.049	0.013	0.268	0.086
Eu	0.025	0.035	0.022	0.033	0.019	6.41	0.235
Gd	0.005	0.006	0.002	0.036	0.008	0.120	0.066
Tb	<0.001	<0.001	0.001	0.001	0.001	0.006	0.002
Dy	0.007	0.007	0.010	0.054	0.013	0.030	0.086
Ho	<0.001	<0.001	0.002	<0.001	0.001	0.017	0.001
Er	0.001	<0.001	0.007	<0.001	0.003	0.164	0.005
Tm	<0.001	<0.001	0.001	<0.001	0.001	0.267	0.001
Yb	0.001	0.001	0.005	0.003	0.004	5.54	0.013
Lu	<0.001	<0.001	0.001	<0.001	0.001	2.23	0.003
ΣREE	0.114	0.145	0.115	0.600	0.220	16.9	1.12
Eu/Eu*	18.7	22.4	33.7	3.48	8.05	159	13.9
Ce/Ce*	0.213	0.230	0.837	0.181	0.283	0.100	0.183
La/Yb	1.8	2.4	0.4	3.1	1.0	0.025	1.1
Nd/Yb	1.7	2.2	0.3	4.1	1.0	0.002	1.5
Yb/Gd	0.3	0.3	0.1	4.0	0.8	74.2	0.3

cerianite (CeO_2) (Braun, 1990) or can be scavenged on the surface of Mn-Fe-oxyhydroxides (Bau, 1999), through sorption of Ce^{3+} together with other REE^{3+}, partial oxidation of Ce^{3+} to Ce^{4+} and preferential desorption of Ce^{3+} and other REE^{3+} compared to Ce^{4+}. Positive Eu anomalies in groundwater can be contributed to positive anomalies in the aquifer sediments through which it flows, it can originate from preferential dissolution of Eu-enriched minerals (e.g., clays and plagioclase) or preferential mobilization of Eu^{2+} during water–mineral interaction compared to the trivalent REEs under reducing conditions (Banks *et al.* 1999; Lee *et al.* 2003; Kharitonov *et al.* 2007; Leybourne and Johannesson 2008, Guo *et al.* 2010). As the investigated thermal waters originate from geologically different aquifers it cannot be excluded that, at least partly, the Eu anomalies are inherited from the source sediments through which they flow. Negative Ce anomalies recorded in all thermal waters argue in favor of partial contribution of Eu from dissolution of Eu-enriched minerals, e.g clays and/or plagioclase, rather than negative redox conditions.

The exception is the thermal water from Bizovka (T6), in which the large positive Eu anomaly (Eu/Eu* = 159) and the large negative Ce anomaly (Ce/Ce* = 0.10) were observed. Large positive Eu anomalies are universally observed in groundwaters with low Eh values, i.e. reducing conditions, due to preferential mobilization of Eu^{2+} compared to the other trivalent REEs. Reducing conditions are generally an important factor that causes elevated concentrations of rare earth and other trace elements in the groundwater. Accordingly, the thermal water from Bizovac (spring Bizovka, T6) contains high concentrations of all rare earth elements (ΣREE = 16.9 μg/L), as well as elevated levels of some trace elements (As, Fe, Ba, Sr, Mn and Li). Development of strongly reducing conditions at near-neutral pH values is reported as one of the major conditions leading to high groundwater As concentrations (Smedley and Kinniburgh, 2002). Such conditions favor the reductive dissolution of Fe and Mn oxide with subsequent release of arsenic and other trace elements. The latter is corroborated by general characteristics of As-rich groundwater from Eastern Croatia (Ćavar *et al.*, 2005; Ujević *et al.*, 2010; Romić *et al.*, 2011). Studies conducted in this area showed that the spatial distribution of As in the groundwater is linked with geological, geomorphological and hydrogeological development of the alluvial basin, and that reductive dissolution of Fe-oxides, desorption of As from Fe-oxides and/or clay minerals as well as competition for the sorption sites with organic matter and PO_4^{3-} could be the principal mechanisms controlling As mobilization (Ujević *et al.*, 2010). Negative cerium anomaly is the general characteristic of oxic conditions in the aquifer, which is in contrast to the high positive Eu anomaly and elevated concentrations of As, Fe, Mn, and other elements in thermal water from T6. However, anomalous La enrichments can create false negative Ce anomaly. In order to distinguish *true* from *false* Ce anomaly Bau and Dulski (1996) suggested ploting of Ce/Ce* vs. Pr/Pr* ($Pr/Pr^* = Pr_{NASC}/(Ce_{NASC} \times Nd_{NASC})$). True negative Ce anomalies are represented by negative Ce/Ce* and positive Pr/Pr*, whereas true positive Ce anomalies are represented by positive Ce/Ce* and negative Pr/Pr*. For thermal water from Bizovka (T6) Pr/Pr* = 4.4 indicates negative Ce anomaly as *true*. The possible explanation for negative Ce anomalie would be that more Ce has been fixed as CeO_2 than adsorbed on Fe oxyhydroxides during sedimentation in an oxic environment. By development of reducing conditions within the aquifer, reduction of Fe oxyhydroxides releases the adsorbed Ce, while reduction of CeO_2 is slower and only gradually mobilizes Ce into the waters (Guo *et al.* 2010). Another plausible explanation would be that negative Ce anomaly in thermal water at T6 was inherited from surrounding host rocks. Starijaš Mayer *et al.* (2014) recently described a monazite with strong negative Ce anomaly from a metadiorite of the nearby Slavonian mountains, explaining the observed anomaly by oxidizing conditions of Cretaceous metamorphism. The Slavonian mountains existed as uplifted paleorelief through entire Neogene in the Pannonian Basin system and consequently supplied, at least partly, surrounding area with material generated through erosion. Concentrations of REE in the analyzed thermal waters, normalized with respect to the estimated average composition of the North American Shale Composite (NASC), (Gromet *et al.* 1984) are presented in Fig. 2.

Observing normalized patterns, we can clearly differentiate thermal waters with regard to their region of origin. Thermal waters from Hrvatsko zagorje (T1, T2 and T3) are characterized by an overall predominance of LREE over HREE ($1.8 < (La/Yb)_{NASC} < 3.1$; $1.7 < (Nd/Yb)_{NASC} < 4.1$, $0.1 < (Yb/Gd)_{NASC} < 0.3$) which is a consequence of the fact that concentrations of elements from gadolinium to lutetium in these samples are very low or below the detection limits. The difference in the intensity of europium anomalies in the thermal waters of the Krapina Spa (T3) in comparison with the other two thermal waters (T1 and T2) is most likely the result of differences in the underlying geology. The REE pattern of thermal water from Varaždin Spa (T4) is characterized by flat, sloping curve caused by an increase in normalized element concentration with an increase in atomic number resulting in an overall predominance of HREE over LREE ($(La/Yb)_{NASC} = 0.4$; $(Nd/Yb)_{NASC} = 0.3$; $(Yb/Gd)_{NASC} = 4.0$). This thermal water also exhibited the lowest negative cerium anomaly (Ce/Ce* = 0.84) and the lowest pH of all studied (pH = 6.8). The preferential release of the HREEs to groundwater and adsorption of the LREEs at sediment particle surfaces are explained by their stronger affinities for the LREEs over the HREEs (Johannesson and Hendry 2000). The shape of the normalized pattern suggests that the geochemical signature of this water is largely controlled by a detrital shale-like component of the aquifer which is confirmed by the relatively high Rb/Cs ratio (5.1). The REE normalized pattern of thermal water from Lipik Spa (T5) shows similarity with thermal waters T1 – T3 from Hrvatsko zagorje. Nonetheless, the HREE are present at higher concentrations in this water and normalized pattern display no predominance of LREE or HREE ($(La/Yb)_{NASC}$ = 1.0, $(Nd/Yb)_{NASC}$ = 1.0, $(Yb/Gd)_{NASC}$ = 0.8). Thermal waters from Bizovac Spa significantly differ from all other studied waters with regard to the REE concentrations as well as the normalized patterns. Similarity with the abovementioned waters was observed only for LREE, while the HREE display sharp increase with the increase in atomic number. This increase was more intense in thermal water from the site T6, which also contains the overall highest concentration of rare earth elements in a way that HREE are predominant over LREE ($(La/Yb)_{NASC}$ = 0.025; $(Nd/Yb)_{NASC}$ = 0.002, $(Yb/Gd)_{NASC}$ = 74.2), which is not the case for the sample from the site T7 ($(La/Yb)_{NASC}$ = 1.1; $(Nd/Yb)_{NASC}$ = 1.5, $(Yb/Gd)_{NASC}$ = 0.3). Observed fractionation between HREE and LREE in thermal water from T6 is too high to be controlled only by speciation fractionation. The extreme enrichments in HREEs compared to LREEs ($(La/Yb)_{NASC}$ = 0.1) in groundwater of Primorye, Russia Shand *et al*. (2005) explained by weathering phase, i.e. zircon, with heavy REE enrichment. Therefore, there is a presumption that the REE pattern of thermal water from the Bizovac Spa (T6) is predominately inherited from the host rock.

CONCLUSIONS

In this paper, the concentrations of 46 elements, including rare earth elements, in Croatian thermal waters, are presented. Studied thermal waters are characterized by broad range of temperatures (30 – 92 °C range), near-neutral to alkaline pH (6.8 – 8.1) and great variability with respect to the levels of trace as well as rare earth elements. Despite a limited sample set, multielemental characterization enabled clear distinction between studied thermal waters and provided information about the underlying geology. Thermal water from Bizovac Spa, from the eastern part of Croatia was found enriched in majority of measured elements in comparison with waters from Hrvatsko zagorje and Lipik. Significant variability between studied thermal waters was observed regarding the REE signatures and fractionation patterns as well. In general, studied thermal waters were found characterized by substantially different normalized REE patterns and wide range of Eu and Ce anomalies, ranging from 0.10 to 0.84 and from 3.48 to 159, respectively.

This study for the first time gives an overview of a large number of elements in thermal waters from Croatian territory and thus represents a starting point for a numerous future studies. The chemical composition of the thermal waters is a result of water-rock interaction processes and this knowledge can be applicable in studies of geochemical, geological as well as hydrogeological characteristics of the deep aquifers.

This study also highlights the benefits of measuring some additional elements, such as the group of rare earths, for a better understanding of fluid dynamics in low-temperature systems, at the same time complementing the characterization and facilitating the interpretation of the factors that influence their composition.

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