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Rare earth elements and yttrium in cold mineral and thermal (~30-60 °C) waters from Tertiary aquifers in the Mura Basin, north-eastern Slovenia: A review

Elementi redkih zemelj in itrij v hladnih mineralnih in termalnih (~30-60 °C) vodah iz terciarnih vodonosnikov Murskega bazena v severovzhodni Sloveniji: pregled dosedanjih raziskav

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Abstract

Cold mineral and thermal waters from Tertiary aquifers in the Mura Basin mainly belong to the Ca-(Mg)-(Na)-HCO_3 and Na-HCO_3 hydrogeochemical facies, respectively, and the concentrations of yttrium (Y) and lanthanides or rare earth elements (REEs) are far below (10^{-2} – 10^{-4}) the abundances in the aquifer sediments. Mineral waters are high pCO_2, and the plots of concentrations of YREEs normalised to Post Archean Australian Shale (PAAS) show fractionation of Y and heavy REEs (HREEs) over light REEs (LREEs), and a significant positive europium (Eu) anomaly. Thermal water from regionally developed aquifer Thermal I (recently also termed the Mura/Ujfalu Formation aquifer) shows a similar PAAS-normalised pattern with an obvious positive Eu anomaly and the tendency of enrichment with middle REEs (MREEs). The plots of PAAS-normalised YREE concentrations in thermal waters from the underlying low-permeability aquifers with poorly developed fracture porosity and abundant CO_2 are flat with insignificant positive Eu anomaly. The abundance and fractionation of YREEs in mineral and thermal waters seems to be mainly controlled by the presence of carbonate complexing ligands, permeability of the aquifers and the related time of water-rock interaction.

YREEs have been used for geochemical recognition of overexploitation of the Sob-1 well that yields mixed waters from Thermal I and the underlying low-permeability aquifers. The well overexploitation has resulted in continuous 30-to-80-minute changes in hydrodynamic pressure in Thermal I, and the related change in temperature and chemical composition of abstracted water. Leakage from clayey-silty layers rich in coal and organic matter has been recognised over a several-year time scale by increased abundances of total organic carbon (TOC), YREEs, gallium (Ga), thallium (Tl) and selenium (Se). PAAS-normalised plots of YREE concentrations have shown significant positive anomalies of samarium (Sm), terbium (Tb) and holmium (Ho) and indicate the YHREE complexing ligands could be, beside carbonate species, humic and/or fulvic acids.

Izvleček

Hladne mineralne vode iz terciarnih vodonosnikov Murskega bazena večinoma pripadajo Ca-(Mg)-(Na)-HCO_3 ali Na-HCO_3 hidrogeokemičnemu faciesu, koncentracije itrija (Y) in lantanoidov oziroma elementov redkih zemelj (REE) pa so za faktor 10^{-2} do 10^{-4} nižje od vsebnosti v prikamnini vodonosnika. Za mineralne vode je značilen visok pCO_2, grafi koncentracij YREE, normaliziranih na vsebnosti Po arhajskega avstralskega skrilavca (PAAS) pa kažejo na frakcionacijo, ki se odraža v sorazmerno višji vsebnosti Y in težkih REE (HREE) glede na lahke REE (LREE), ter na značilno visoko pozitivno evropijevo (Eu) anomalijo. Termalne vode iz vodonosnika Termal I, ki je razvit v globinah Murskega bazena, kažejo podobno grafično razporeditev na PAAS normaliziranih koncentracij YREE z jasno izraženo pozitivno Eu anomalijo in težnjo po obogatitvi s srednjimi REE (MREE). Grafi na PAAS normaliziranih koncentracij YREE v termalnih vodah iz vodonosnikov, ki leže pod Termalom I in ki imajo nizko prepustnost in slabo razvito razpoklinsko poroznost ter so bogati s plinom CO_2, pa so bolj ravni s komaj zaznavno pozitivno Eu anomalijo. Vsebnosti in frakcionacija YREE v mineralnih in termalnih vodah je najverjetneje odvisna od prisotnosti karbonatnih ligandov, prepustnosti vodonosnika in časa interakcije vode in prikamnine.

YREE so se izkazale kot dober pokazatelj prekomernega izkoriščanja vrtine Sob-1, kjer so bile zajete vode iz Termala I in slabo prepustnih vodonosnikov pod njim. Prekomerno izkoriščanje vrtine je imelo za posledico zvezno ciklično spreminjanje hidrodinamičnega tlaka v Termalu I, s hkratnim spreminjanjem temperature in kemijske sestave vode v časovnih intervalih 30-80 minut. Izcejanje iz glinasto-meljastih plasti bogatih z lečami premoga in organske snovi smo zaznali v časovnem obdobju več let kot povečanje vsebnosti celokupnega organskega ogljika (TOC), YREE, galija (Ga), talija (Tl) in selena (Se). Grafi na PAAS normaliziranih koncentracij YREE so pokazali visoke pozitivne anomalije samarija (Sm), terbija (Tb) in holmija (Ho) in kažejo, da so bile poleg karbonatnih ligandov v kompleksnih spojinah YHREE najverjetneje pomembne tudi huminske in/ali fulvične kisline.

Introduction

The series of lanthanides or rare earth elements (REEs) and yttrium (Y) - here abbreviated as YREEs, have been recognised exceptionally important in various aspects of hydrogeochemical research. The early studies refer to marine waters and hydrothermal vents associated with mid-ocean spreading centres (Elderfield & Greaves, 1982; DeBaar et al., 1985; 1988; Klinkhammer et al., 1994; Bau & Dulski, 1999; Douville et al., 1999; 2002) while in continental areas, the abundances of REEs were first investigated in thermal waters in France and the Himalayas (Michard & Albarède, 1986; Michard et al., 1987; Michard, 1989). REEs have been used as geochemical tracers in several studies of groundwater regional flow and mixing (e.g., Johannesson et al., 1996; 1997; 2000; 2005; Dia et al., 2000; Tweed et al., 2006; Möller et al., 2007; Biddau et al., 2009; Yuan et al., 2014; Liu et al., 2017), exploration of power-producing geothermal systems and identification of potential high-level nuclear waste repositories (Möller, 2000; Shannon et al., 2001; van Middlesworth & Wood, 1998; Möller et al., 2003; Wood, 2006). During the past four decades the potential of REEs as environmental pollutants exponentially increased as they have become indispensable in several sectors of modern industry such as clean-energy, electronics or military, and have been utilised in a number of medical, agricultural and zootechnical applications (e.g., Möller et al., 2000; Kulaksiz & Bau, 2011; Hissler et al., 2014; Gonzales et al., 2014; Hatje et al., 2016; Nigro et al., 2018; Aide, 2018; Ladonin, 2019).

The utility of REEs as geochemical tracers is based on their conservative behaviour in many natural systems although several processes related to the REE aqueous chemistry can cause their fractionation. The most important are solubility and precipitation of REE hosting minerals, REE chemical speciation and complexation in solution and on mineral surfaces, ion distribution in the electric double layer attached to mineral surfaces, the changes in pH, redox conditions and temperature of the aqueous medium, and hydrogeological factors such as flow pathways or residence time (Brookins, 1989; Wood, 1990; Drever, 1997; Möller, 2000). Furthermore, while REEs exist mostly in trivalent state, europium Eu^{3+} and Ce^{3+} can be reduced or oxidised to Eu^{2+} and Ce^{4+}, respectively (Sverjensky, 1984; Smedley, 1991; Bilal, 1991; Bau, 1991; 1999; Johannesson et al., 1996; Liu & Byrne 1998). REEs, especially heavy rare earth elements (HREEs), are known for their affinity to form strong solution complexes with carbonate ions and are commonly relatively enriched in CO_2-rich cold mineral or thermal waters although surface complexation can reduce their abundance in solution (Cantrell & Byrne, 1987; Lee & Byrne, 1993; Michard et al., 1987; Guo et al., 2005; Shand et al., 2005).

Absolute concentrations of REEs are highly variable in natural waters and they are customary displayed as plots of normalised values on a logarithmic scale versus atomic number or ionic radius on a linear scale (Coryell et al., 1963). Yttrium is plotted at about the position of holmium (Ho). Commonly used datasets for normalisation are C1-chondrite (Anders & Grevesse 1989) and Post Archean Australian Shale (PAAS, McLennan, 1989) as the use of such reference materials enables easy comparison of large number of analyses worldwide. Recently, an improved data set for the European Shale has been proposed for environmental studies in Europe (Bau et al., 2018). Sometimes reservoir rocks are used in order to obtain more specific information on water-rock interaction, pathways of flow or mixing of waters.

In Slovenia, the first study on REE abundances in natural waters has been related to thermal and mineral waters in the Mura Basin, north-eastern Slovenia (Kralj & Kralj, 2000a), and up to the present, an upgraded and extended research of this topic has been the only available source of data (Kralj & Kralj, 2000b; 2009; 2012; Kralj, 2001; 2004a). In the end of the year 2021, a common Slovenian-Austrian project on geochemistry of water and stream sediment of the river Mur started (https://www.geo-zs.si/index.php/projekti/drugi-projekti; https://aach.

unileoben.ac.at/en/news). The project has been termed MURmap, and the research is focused on classical heavy metal (HM) pollutants and technology-critical elements (TCEs), including YREEs. Therefore, a need for critical review of state-of-the-art of research of YREEs in natural waters and sediments in north-eastern Slovenia occurred, and that is the primary aim of the present contribution.

North-eastern Slovenia forms a part of the Pannonian Mura Basin (Fig. 1) which has been known for centuries for sources of mineral and thermal water. During the past five decades, thermal water from a particular intergranular aquifer named Thermal I (and recently also the Mura/Ujfalu Formation aquifer) has become a basis of economically important spa tourism in the area (Žlebnik et al., 1988a; b; Ravnik et al., 1992; Kralj, 1993; 1994; 1995; 2001; Rman, 2014; Szőcs et al., 2018). Mineral waters are high pCO_2 and belong to the $Na\text{-}Ca\text{-}HCO_3$, $Ca\text{-}Na\text{-}HCO_3$, $Ca\text{-}Mg\text{-}Na\text{-}HCO_3$ or $Ca\text{-}Mg\text{-}(Na)\text{-}HCO_3$ hydrogeochemical facies. The plots of PAAS-normalised concentrations of YREE in mineral waters are characterised by high positive Eu anomalies and the enrichment of heavy REEs (HREEs) over light REEs (LREEs), (Kralj & Kralj, 2000a).

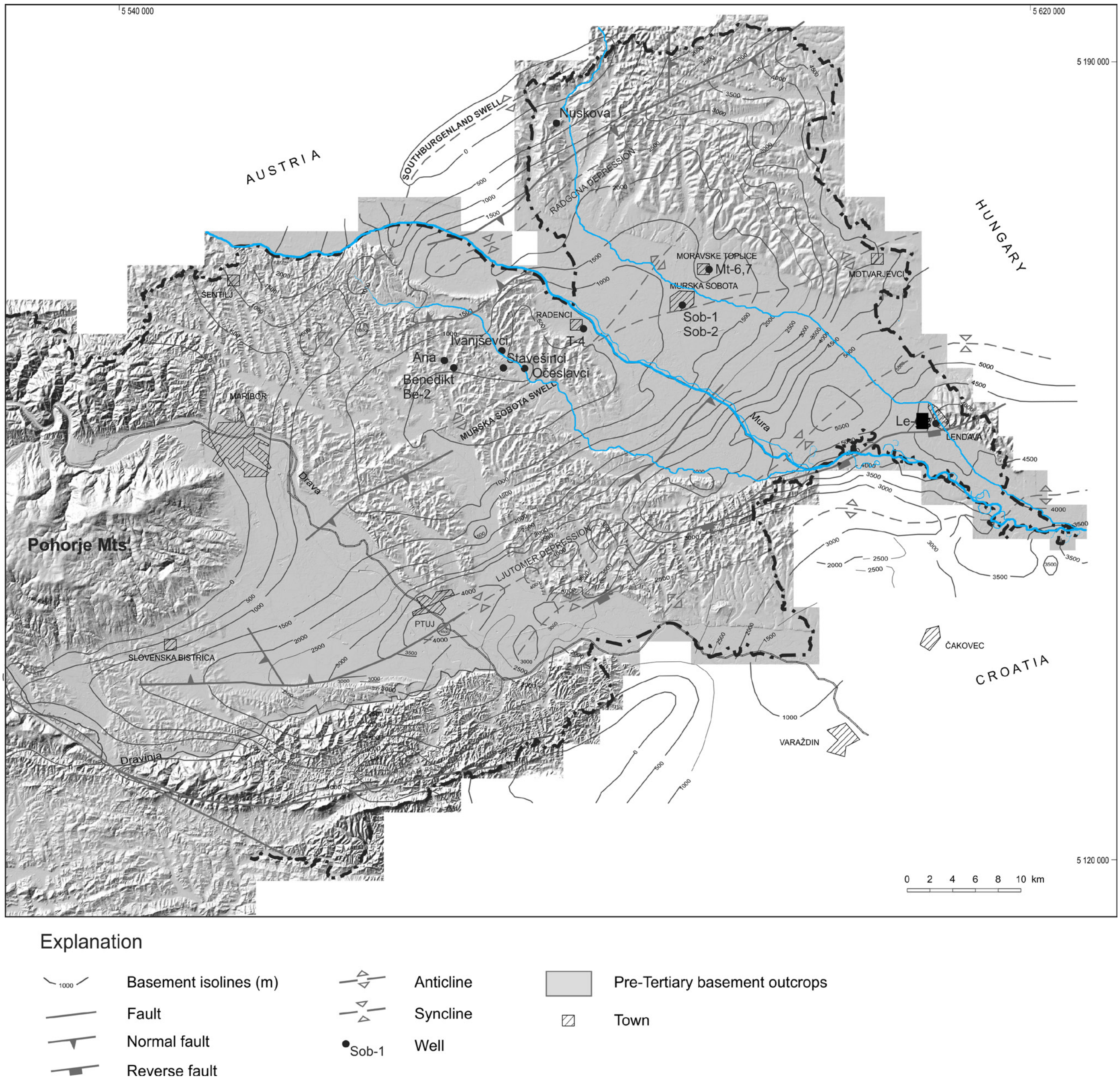

Fig. 1. Structural map of the Mura Basin and geographic position of the discussed geothermal wells, and springs and shallow drill-holes capturing mineral waters (modified after Rajver et al., 1994; Kralj & Kralj, 2000a; 2012). Recent geological models (e.g., Šram et al., 2015) use modified naming of geological structures in comparison to those listed in the present contribution.

Thermal waters are low- to medium-temperature (~30-60 °C) and essentially belong to the Na-HCO_3 hydrogeochemical facies. The abundances of YREEs and their PAAS-normalised patterns are not uniform, and for the water from Thermal I they resemble those of mineral waters. Thermal waters from poorly fractured aquifers in the Lendava, Haloze and Špilje Formations have higher concentrations of YREEs and their PAAS-normalised plots are flatter. From the wells Sob-1 and Sob-2, a mixture of thermal waters from Thermal I and several underlying low-yield aquifers in the Lendava Formation has been produced, and the plots of PAAS-normalised YREE concentrations are specific owing to temporal variations of chemical composition of abstracted mixture of thermal waters (Kralj, 2004a; b; Kralj & Kralj, 2009; 2012).

In the present contribution the significance of YREEs in recognition of water-rock interaction, well overexploitation and mixing of waters from various aquifers in the Tertiary sedimentary succession of the Mura Basin is discussed. Abundant analytical data, normalisation technique using various materials and its interpretation have been included in the article in order to serve as a basis for future studies of YREEs in natural waters and sediments in the Mura Basin and also broader, the catchment area of the river Mur.

Analytical techniques

The measurements of pressure and temperature in the aquifer Thermal I were performed in the Sob-1 well simultaneously with, i) Amerada-type survey clock with mechanical temperature and pressure recorder, and ii) Leutert pressure-temperature gauge having a resolution of 0.007 bar and 0.01 °C, with measurements taken every 10 seconds and computer-managed data output. In the Sob-1 well, the measurements have been performed in the years from 1990 to 1999, at a depth of 600 m, four times a year in a period of one week. Since September 1995, the well-head water temperature (± 0.3 °C), electrical conductivity (± 0.5 % of the measured value), pH (± 0.1 unit), redox potential Eh (± 0.3 mV) and dissolved oxygen DO (± 0.5 % of the measured value) were measured at the well-head using WTW MultiLine P3 pH/LF/Oxymeter portable instrument.

In the same week, water samples were collected from the well-head outflow using pre-cleaned polyethylene bottles of one-liter and two-deciliter volumes for the analysis of major ions and minor ions/elements, and trace elements, respectively. The bottles were rinsed three times with the sampled water, and for the analysis of trace elements the samples were acidified by ultrapur HNO_3 (Merck) to pH<2 without prior filtration. After collection, the samples were sent immediately in the laboratories.

The major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, SO_4^{2-}), minor ions/elements (F^-, J^-, Br^-, NH_4^+, Fe, Mn), the dissolved CO_2-gas and total organic carbon (TOC) were determined in 95 samples. The concentrations of major cations were analysed by ion chromatography (IC). The concentration of bicarbonate was determined by potentiometric titration using 0.1 N HCl. The chloride and fluoride ions were analysed by IC and ion-selective electrode (ISE), respectively, and the bromide and iodide ions by Inductively Coupled Plasma Source Emission Spectroscopy combined with Mass Spectroscopy (ICP-MS). The charge balance between the sum of milliequivalent concentrations (meq/L) of major anions and cations

$$((\Sigma[\text{Anions}]-\Sigma[\text{Cations}]/(\Sigma[\text{Anions}]+\Sigma[\text{Cations}]))$$

was assessed and the analyses with deviations of <5 % accepted.

Trace elements Li, Be, B, Al, Sc, Ga, As, Se, Rb, Sr, Tl, Y and REEs (along with V, Cr, Co, Ni, Cu, Zn, Zr, Nb, Mo, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, Hf, Ta, W, Hg, Pb, Bi, Th and U that are not discussed in this paper) have been determined in 36 samples of thermal water from the Sob-1 well that were collected from May 1997 to June 1999. Trace elements were analysed in X-RAL Activation Services Inc., Ann Arbor, Michigan, the United States of America. The abundances of Y and REE were determined by ICP/MS (inductively coupled plasma source emission spectroscopy combined with mass spectroscopy) techniques without using any preconcentration method such as solid phase extraction, solvent extraction (e.g., Shannon & Wood, 2005) or coprecipitation with iron hydroxide (Zhu et al., 2010).

From June 1988 till December 1996, the samples of thermal water from the Sob-2 well have been collected in the same time period, and the sampling and analytical procedure performed in the same manner as for thermal water from the Sob-1 well. Major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, SO_4^{2-}), minor ions/elements (F^-, J^-, Br^-, Fe, Mn), the CO_2-gas and total organic carbon (TOC) were determined in 53 samples. In October 1998 and June 1999, altogether 8 samples were collected for the analysis of major ions, minor ions/elements, the CO_2-gas, TOC and trace elements including Y and REEs.

The same well-head measurements of water temperature, pH, Eh, conductivity and DO, and sampling procedure and analytical technique for determination of major ions, minor ions/elements, the gases CO_2 and H_2S, TOC and trace elements as carried out for thermal water from the Sob-1 well were applied for thermal waters from the wells Le-2g and T-4, and mineral waters from shallow drill-holes/walled springs at Benedikt, Nuskova, Ivanjševci, Očeslavci, and Stavešinci. In each thermal well and drill-hole/walled spring 3 and 1 samples, respectively, were collected.

The abundances of major oxides and trace elements in Tertiary sediments including Y and REE were determined in ACME analytical Laboratories, Vancouver, Canada. The analysis of trace elements was performed using ICP/MS and XRF (X-ray fluorescence) techniques. Mineral composition of aquifer sediments was determined by X-ray diffraction analysis of powdered samples using Philips diffractometer PW 3719 and goniometer PW 1820 owned by the Department of Geology, Faculty of Natural Sciences and Technology, University of Ljubljana. Digital data were processed with peak-fitting program X'Pert HighScore Plus 4.0.

Geological setting

The most important tectonic structure in north-eastern Slovenia is the Mura Basin (INA-Projekt Zagreb & Geološki zavod Ljubljana, 1991) which has been also considered as a part of much larger structural complexes of the southern Pannonian Basin System, namely, of the Mura-Zala Basin (sensu Fodor et al., 2002; Jelen et al., 2006) and the Zala-Drava Basin (e.g., Royden, 1988; Malvić & Velić, 2011), respectively. In the west, the Mura Basin terminates along the Pohorje Mountains that belong to the Eastern Alps (Fig. 1) and deepens toward the east where it reaches maximum depths of over 4 km in some isolated compartments near the Slovenian-Hungarian border. The formation of the Mura Basin begun in Late Ottnangian as a result of continental rifting and the following extension and subsidence along two fault zones, more specifically, the Raba Fault in the north and the Ljutomer Fault in the south. The faults have regional extent and they evolved into the Radgona-Vas and Haloze-Ljutomer-Budafa sub-basins (Fodor et al., 2002; Márton et al., 2002; Jelen & Rifelj 2011). The sub-basins have been separated by the Murska Sobota Swell (INA-Projekt Zagreb & Geološki zavod Ljubljana, 1991).

Pre-Tertiary basement of the Mura Basin consists of Paleozoic metamorphic rocks, Upper Carboniferous and Lower Permian sedimentary deposits, and rare erosional remnants of Triassic dolomite and limestone (Koščec & Jovanović, 1968). The oldest Neogene deposits are Ottnangian fluvial-limnic and Lower Badenian marine deposits, and the successions are united in the Haloze Formation. Sarmatian to Early Pannonian depositional environment was brackish. Sarmatian deposits are developed as well compacted and partially lithified sand, silt, clayey silt and marl, and Lower Pannonian sediments are dominated by silt, siltstone, fine-grained sand and marl. The successions are united in the Špilje Formation (Rijavec et al., 1985; Jelen et al., 2006). During Late Miocene, the Mura Basin became a part of extensive Lake Pannon. The environment gradually changed from brackish to freshwater owing to its isolation from Western Parathetys and advance of fluvial systems draining the Eastern Alps (Rijavec et al., 1985; Piler et al., 2007; Kováč et al., 2017). Deltaic systems developed and fine-grained turbidites fed from delta slopes form the Middle Pannonian to Lower Pontian Lendava Formation. Delta front and delta plain deposits are united in the Upper Pannonian to Upper Pontian Mura Formation. The overlying Dacian and Romanian deposits are related to the systems of alluvial fans and braided rivers (Kralj, 2010), and the successions are united in the Ptuj-Grad Formation (Jelen & Rifelj 2011; Nádor et al., 2012; Šram et al., 2015). Some 3 My ago, alkali basaltic volcanism occurred in the vicinity of the South Burgenland Swell and produced a variety of volcanic and mixed volcaniclastic-fluvial deposits (Pleničar, 1968; Kralj, 2010).

Cold mineral waters spring out along the margins of the Radgona Depression at the place of Benedikt and the village of Nuskova (Fig. 1), and in the Ščavnica valley (Stavešinci, Ivanjševci, Očeslavci) just above the westernmost extending of the Murska Sobota Swell (e.g., Kralj & Kralj, 2000; Gabor & Rman, 2016). In the area Badenian and Sarmatian deposits of the Haloze and Špilje Formations outcrop, and deep-seated faults enable uplift of the CO_2-gas from pre-Tertiary basement.

In the Mura Basin, thermal aquifers occur in pre-Tertiary basement, and in Haloze, Špilje, Lendava, Mura and Ptuj-Grad Formations (Fig. 2), (Kralj, 2001; Nádor et al., 2012; Šram et al., 2015). Pre-Tertiary aquifers are commonly fractured or cavernous. In the deepest confined and semi-confined compartments brines of essentially Na-Cl composition prevail, and in some shallower carbonate aquifers thermal waters of the Na-HCO_3, Na-HCO_3-Cl or Na-SO_4-HCO_3 hydrogeochemical facies have been encountered (Kralj, 1993; 1994; Kralj & Kralj, 2000a). In the Haloze and Špilje Formations low-permeability thermal aquifers occur and chemical composition of waters depends on their depth and paleoenvironmental conditions that locally enabled infiltration of younger fresh-waters. The amount of total dissolved solids commonly exceeds 10 g/L (Szocs et al., 2013) and the CO_2-gas is common (INA-Projekt Zagreb & Geološki zavod Ljubljana, 1991; Kralj, 2001). In the Lendava Formation isolated aquifers occur (Szocs et al., 2013), the yield of thermal water is low, and the CO_2-gas originating from lithospheric mantle (Bräuer et al., 2016) is abundant. The waters have high amount of total dissolved ions (TDI) that commonly exceeds 10 g/L, and they essentially belong to the Na-HCO_3 hydrogeochemical facies (Table 1, T-4). The concentrations of the Ca^{2+}, K^+ and Mg^{2+} may be much higher than in the waters from pre-Tertiary basement (Kralj & Kralj, 2000a; Szocs et al., 2013).

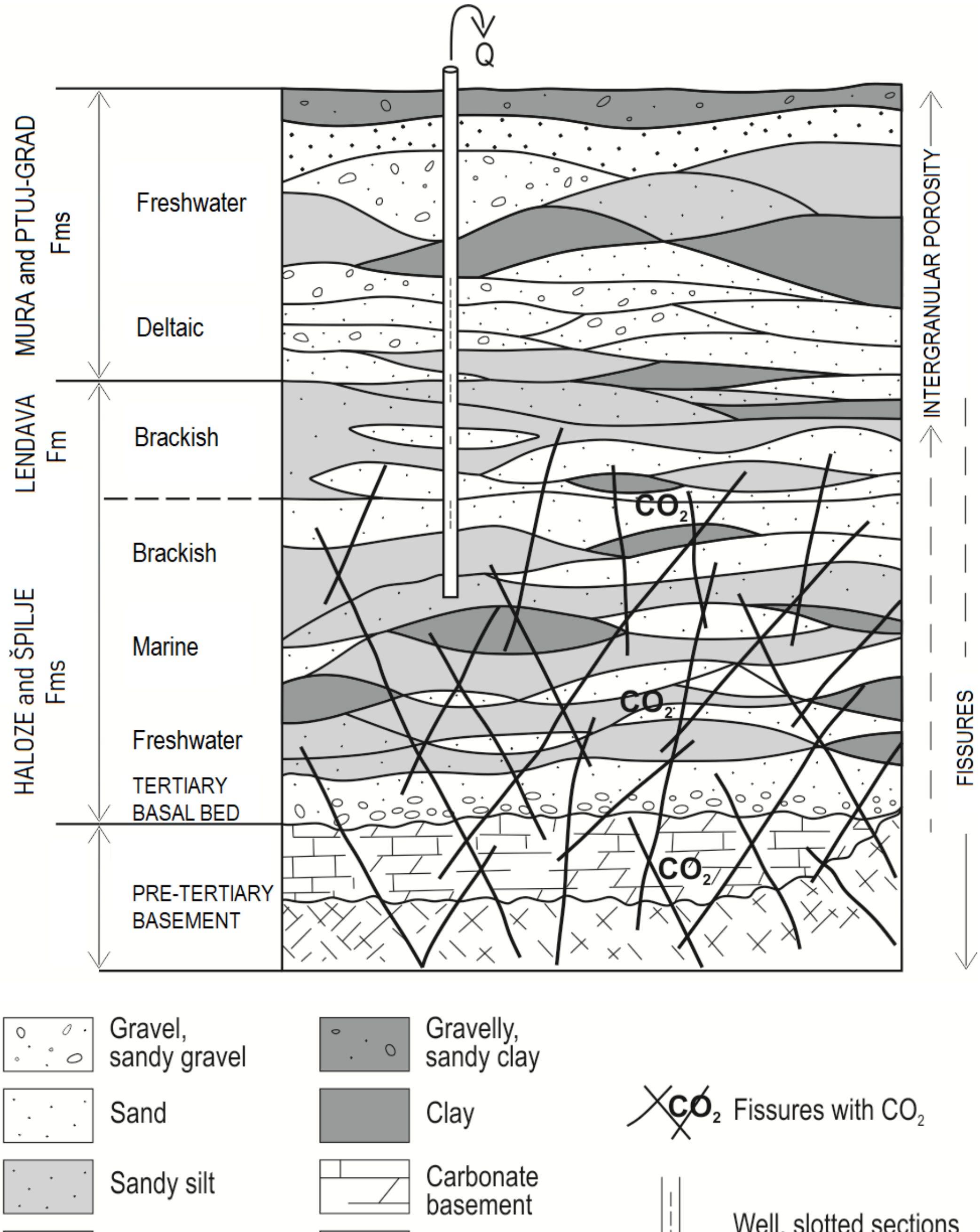

Fig. 2. Idealised model of sedimentary formations with thermal aquifers in the Mura Basin and a typical productive well capturing waters from several thermal aquifers (modified from Kralj, 2001). The names of formations are adopted from Jelen et al., 2006.

Table 1. Average chemical composition of thermal waters; major ions, minor ions/elements, dissolved CO_2-gas, dissolved silica (SiO_2), total organic carbon (TOC), total dissolved ions (TDI), pH, temperature of water at well-head (T_{wh}) and yttrium and rare earth elements (YREEs). The wells T-4 (Radenci), Sob-1 and Sob-2 (Murska Sobota) and Le-2g (Lendava) tapped thermal aquifers in the Haloze, Špilje and Lendava Formations, Lendava and Mura Formations, and Mura Formation, respectively. For the Sob-1 and Sob-2, low-TDI and high-TDI indicate 30-to-80-minute variations of chemical composition (also referred as well cycling), and low and high pumping rate, respectively.

Well		Le-2g*	Sob-1*	Sob-1 (low-TDI)	Sob-1 (high-TDI)	Sob-2*	Sob-2 (low-TDI)	Sob-2 (high-TDI)	T-4*
Average		3	71	1	1	46	1	1	3
Ion/Oxide/ Parameter	Unit								
Na^+	mg/L	280	731	450	970	653	300	1,100	2,087
K^+	mg/L	7.8	92	70	105	39	31	52	440
Ca^{2+}	mg/L	5.3	37.0	15	71	12.2	7	18	233
Mg^{2+}	mg/L	7.7	8	5	7	3.7	4.0	2	147
Fe	mg/L	0.28	0.15	0.06	0.21	1.12	0.15	0.12	0.047
Mn	µg/L	9	13	6	21	8	7	69	72
Br^-	mg/L	0.11	0.61	0.45	0.92	0.9	0.41	1.52	0.80
J^-	mg/L	<0.01	0.16	0.10	0.09	0.34	0.08	0.67	0.17
F^-	mg/L	0.53	0.78	0.45	0.75	1.40	0.20	0.55	0.84
Cl^-	mg/L	3.3	141	95	175	117	85	180	133
HCO_3^-	mg/L	856	2,214	1,500	2,900	1,645	960	2,600	7,633
SO_4^{2-}	mg/L	2	30	12	48	7	13	2	233
CO_2	mg/L	1	677	440	869	303	88	713	1,476
SiO_2	µg/L	14	18	14	19	15	3	26	32
TOC	mg/L	2.4	2.5	2.5	2.0	5.1	2.5	5.5	2.3
TDI	mg/L	1,173	3,263	2,165	4,300	2,491	1,407	3,989	10,939
pH		7.30	7.0	6.81	6.85	7.9	7.02	6.78	6.85
T_{wh}	°C	58.3	49.0	48.7	49.1	46.6	45.8	47.4	29.8
La	µg/L	0.03	0.19	0.04	1.09	0.06	0.02	0.14	0.39
Ce	µg/L	0.02	0.27	0.06	2.21	0.08	0.03	0.23	0.82
Pr	µg/L	<0.01	0.04	0.01	0.27	0.02	0.01	0.05	0.11
Nd	µg/L	0.02	0.17	0.06	1.08	0.07	0.02	0.17	0.42
Sm	µg/L	0.03	0.11	0.05	0.21	0.10	0.04	0.21	0.18
Eu	µg/L	0.04	0.99	0.07	0.08	0.12	0.06	0.20	0.08
Gd	µg/L	0.03	0.08	0.03	0.24	0.08	0.02	0.16	0.19
Tb	µg/L	0.01	0.13	0.06	0.03	0.02	0.01	0.04	0.01
Dy	µg/L	0.03	0.05	0.04	0.13	0.06	0.02	0.09	0.16
Y	µg/L	0.03	0.29	0.10	0.75	0.10	0.03	0.19	0.79
Ho	µg/L	<0.01	0.08	0.01	0.03	0.02	0.01	0.03	0.01
Er	µg/L	0.02	0.04	0.03	0.06	0.04	0.01	0.10	0.09
Tm	µg/L	0.01	0.01	0.01	0.01	0.02	<0.01	0.03	<0.01
Yb	µg/L	0.02	0.03	0.03	0.04	0.05	<0.01	0.11	0.07
ΣYREEs	µg/L	<0.30	2.48	0.60	6.23	0.84	<0.28	1.75	3.32

*data from Kralj, 2004a and Kralj & Kralj, 2009

The Mura Formation comprises a subsurface interconnected delta-front sand body that developed into thermal aquifer (Nádor et al., 2012; Šram et al., 2015; Tóth et al., 2016) locally termed Thermal I (INA-Projekt Zagreb & Geološki zavod Ljubljana, 1991; Ravnik et al., 1992; Kralj, 2001; Kralj & Kralj, 2012). In the Mura Basin Thermal I encompasses a subsurface area of about 1,372 km^2 (Kralj, 1995; Kralj & Kralj, 2000a, b; 2012; Kralj, 2001; Rajver et al., 1994) although it extends on the territory of Hungary, Austria, Slovakia and Croatia as a large transboundary thermal groundwater body (TTGWB) occupying a subsurface area of over 22,128 km^2 (Nádor et al., 2012; Szocs et al., 2013; Rman, 2014; Šram et al., 2015; Tóth et al., 2016; Rotár-Szalkai et al., 2017; Szőcs et al., 2018).

Thermal I outcrops in the west of the Mura Basin near the town of Radenci and deepens toward the east reaching a depth of over 1000 m at the Slovenian-Hungarian border. In general, the waters belong to the Na-HCO_3 hydrogeochemical facies, TDI commonly ranges from 1,000 – 1,500 mg/L, and free CO_2 is practically absent. Isotopic studies indicate the Pleistocene age of waters from the Mura Formation and the replacement of formation waters by infiltration has been assumed (Szocs et al., 2013). At greater basin's depths where Thermal I is underlain by thick deposits that still belong to the Mura Formation, the concentrations of the chloride ions are low (Table 1, Le-2g). In places where the underlying deposits are thin and/or tectonically displaced, some thermal waters seem to have naturally admixed minor quantities of waters from the Lendava Formation, and as a result, the concentrations of the chloride ions are higher (Table 1, Sob-1 and Sob-2). In the Sob-1 and Sob-2 wells chemical composition of abstracted water has varied in time owing to the well overexploitation (Kralj & Kralj, 2000b; 2012). Recently, hydrogeochemistry, mixing of waters and well cycling and overexploitation during several-year period have been recognised by changes in the abundance of halide ions (Kralj & Kralj, 2020).

Table 2. Chemical composition of mineral waters; major ions, dissolved CO_2-gas, dissolved silica (SiO_2), total organic carbon (TOC), total dissolved ions (TDI), pH and yttrium and rare earth elements (YREEs). Data from Kralj & Kralj, 2000.

Ion/Oxide/ Parameter	Unit	Benedikt Ana	Ivanjševci	Očeslavci	Stavešinci	Nuskova
Na^+	mg/L	51	104	685	162	276
K^+	mg/L	21	15	65	13	3
Ca^{2+}	mg/L	800	487	417	375	328
Mg^{2+}	mg/L	180	203	69	32	47
Fe	mg/L	7.2	6.7	1.2	2.7	0.9
Mn	mg/L	0.170	0.143	0.178	0.359	0.428
J^-	mg/L	<0.01	0.02	0.21	0.05	0.02
F^-	mg/L	0.04	<0.01	0.78	0.22	0.40
Cl^-	mg/L	3	7	170	25	32
HCO_3^-	mg/L	3,400	2,590	2,970	1,690	1,790
SO_4^{2-}	mg/L	23	2	118	19	68
CO_2	mg/L	1,830	2,500	3,800	3,300	3,300
SiO_2	µg/L	43	18	15	17	11
TOC	mg/L	1.3	0.9	0.8	0.6	0.9
TDI	mg/L	4,536	3,420	4,499	2,321	2,547
pH		6.37	6.22	6.22	6.02	6.00
La	µg/L	0.07	0.02	0.06	0.10	0.11
Ce	µg/L	0.14	0.01	0.01	0.15	0.19
Pr	µg/L	0.02	<0.01	<0.01	0.02	0.02
Nd	µg/L	0.08	<0.01	0.09	0.12	0.10
Sm	µg/L	0.06	<0.01	0.02	0.02	0.02
Eu	µg/L	0.17	0.21	0.04	0.08	0.03
Gd	µg/L	0.01	0.01	<0.01	0.05	0.02
Tb	µg/L	0.01	<0.01	<0.01	0.01	0.01
Dy	µg/L	0.02	<0.01	0.01	0.08	0.02
Y	µg/L	0.24	0.70	0.03	1.00	0.28
Ho	µg/L	0.01	<0.01	<0.01	0.02	0.01
Er	µg/L	0.03	0.01	0.01	0.07	0.04
Yb	µg/L	0.02	<0.01	<0.01	0.05	0.02
ΣYREEs	µg/L	0.87	<1.03	<0.32	1.84	0.86

Rare earth elements and yttrium in cold mineral and thermal waters

Cold mineral waters

Cold mineral waters belong to the Na-Ca-HCO_3, Ca-Na-HCO_3, Ca-Mg-Na-HCO_3 or Ca-Mg-(Na)-HCO_3 hydrogeochemical facies. The amount of total dissolved ions (TDI) is variable and ranges from about 2,300 mg/L to over 4,500 mg/L (Table 2). The waters are high pCO_2 and in the analysed samples, the amount of dissolved carbon dioxide ranges from 1,800 to 3,800 mg/L. The concentrations of the chloride and sulphate ions are generally low and the highest recorded were in the spring Očeslavci where they amounted to 170 mg/L and 118 mg/L, respectively. The content of YREE ranges from <0.32 µg/L to 1.84 µg/L and is not proportional to TDI or the amount of dissolved CO_2-gas.

To compare YREE concentrations in cold mineral waters normalised to PAAS and aquifer sediment, Sarmatian calcareous siltstones, the Špilje Formation, from the well Be-2/03, Benedikt at a depth of 122-124 m, have been used (Kralj et al., 2009). The abundances of YREEs in the aquifer sediment show a proportional depletion with the increase in calcite present either as cement, microfossils or limestone lithic fragments (Table 3).

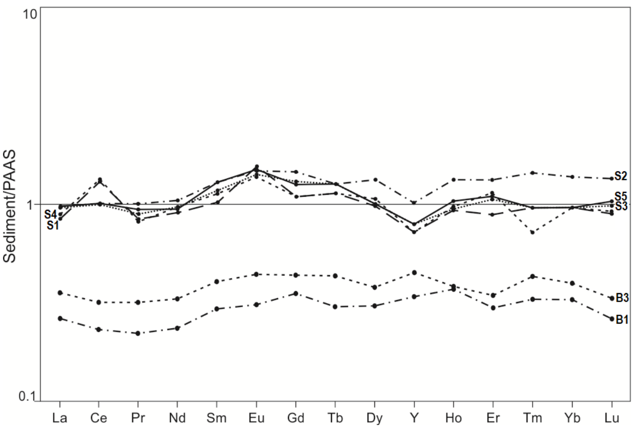

Fig. 3. The plots of PAAS-normalised YREE abundances in aquifer sediments from the wells Be-2/03, Benedikt (B1, B3) and Sob-1, Murska Sobota (S1-S5). For detailed information see Table 3.

The PAAS-normalised plots are alike (Fig. 3) but well below the shale abundance, and MREEs and HREEs are slightly fractionated over LREEs. The plots of YREE concentrations in mineral waters normalised to PAAS and to the average of 3 aquifer sediments do not differ significantly in the shape but only in the magnitude of about $<10^{-1}$ (Fig. 4). They are characterised by fractionation of YHREEs over LREEs and a significant positive Eu anomaly, while Ce anomaly is absent or slightly negative.

Table 3. YREEs in aquifer sediments and PAAS (after McLennan 1989). B1-B3, Špilje Formation, the well Be-2/03, Benedikt; S1-S5, Mura and Lendava Formations, well Sob-1, Murska Sobota.

Sample/ Well Depth	Sediment Type	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu
B1 Be-2/03 122-124 m	Siltstone (30 wt.% $CaCO_3$)	10.0	18.3	1.94	7.9	1.6	0.33	1.62	0.23	1.40	9.0	0.36	0.83	0.13	0.90	0.11
B2 Be-2/03 122-124 m	Siltstone (25 wt.% $CaCO_3$)	13.5	25.1	2.78	11.1	2.2	0.47	2.01	0.33	1.74	11.9	0.37	0.96	0.17	1.09	0.14
B3 Be-2/03 122-124 m	Siltstone (8 wt.% $CaCO_3$)	31.8	63.1	7.05	27.9	5.6	1.10	4.73	0.64	4.16	20.8	0.81	1.95	0.25	2.10	0.33
S1 Sob-1 633 m	Sand	32.9	106.0	7.6	31.6	5.8	1.72	5.2	0.9	4.7	20	0.95	2.6	0.4	2.8	0.40
S2 Sob-1 802 m	Sand	38.4	81.0	9.1	36.1	7.4	1.93	6.9	1.0	6.4	28	1.35	3.9	0.6	4.0	0.60
S3 Sob-1 802 m	Silt	37.6	80.9	8.6	33.7	6.7	1.56	6.2	1.0	4.8	22	0.96	3.1	0.4	2.8	0.44
S4 Sob-1 853 m	Silty sand	34.4	109.0	7.4	33.8	6.4	1.52	5.2	0.9	5.1	20	0.99	3.0	0.3	2.8	0.41
S5 Sob-1 853 m	Silt	38.2	82.3	8.5	32.8	7.3	1.67	6.0	1.0	4.8	22	1.05	3.2	0.4	2.8	0.46
PAAS	Shale	38.2	79.6	8.83	33.9	5.55	1.08	4.66	0.774	4.68	27	0.991	2.85	0.405	2.82	0.443

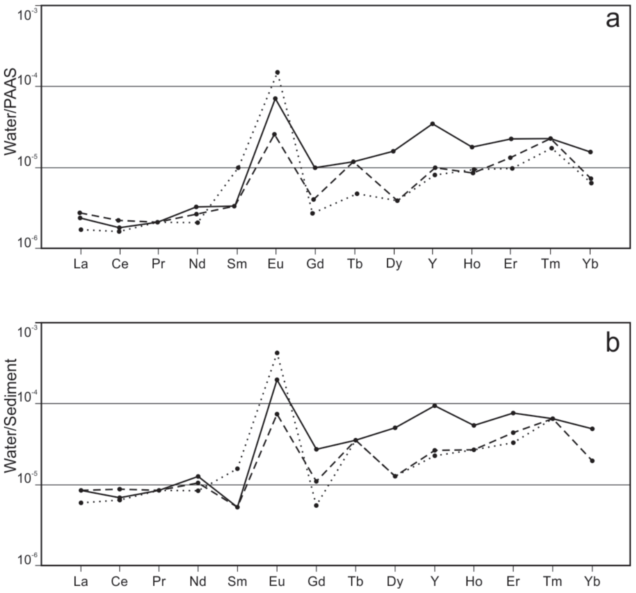

Fig. 4. a, The plots of PAAS-normalised YREE concentrations in mineral waters; b, The plots of concentrations of YREEs in mineral waters normalised to the average of 3 aquifer sediments from the well Be-2/03, Benedikt (122-124 m). Solid line – Stavešinci, dotted line - Ana (Benedikt), dashed line – Nuskova.

Thermal waters from the T-4, Le-2g, Sob-1 and Sob-2 wells

Thermal water from the T-4 well in the town of Radenci belongs to the Na-HCO_3 hydrogeochemical facies and is abstracted from a depth of 400-540 m in the Haloze and Špilje Formations. TDI and the dissolved CO_2-gas amount to nearly 11 g/L and 1.5 g/L, respectively (Table 1), and the sum of YREE concentrations averages to 3.32 µg/L. The plots of PAAS-normalised YREE abundances in the water have shown that MREEs and YHREEs are slightly fractionated over LREEs, and there are very small negative Ce and moderate positive Eu anomalies (Fig. 5).

The well Le-2g in the town of Lendava penetrated Thermal I at a depth of 825-950 m and captures some underlying aquifers in the Mura Formation at a depth interval of 970-1,500 m as well. The water belongs to the Na-HCO_3 hydrogeochemical facies, TDI amounts to about 1.2 g/L and the dissolved CO_2-gas is practically absent (Table 1). The sum of YREEs averages to < 0.28 µg/L, and the plots of PAAS-normalised values show small negative Ce and moderate positive Eu anomalies, and fractionation of MREEs and HREEs over LREEs (Fig. 5).

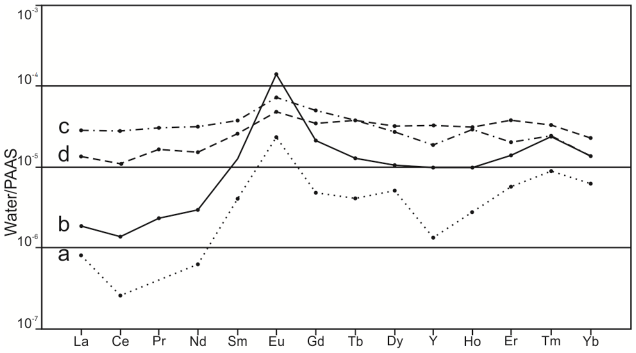

Fig. 5. The plots of PAAS-normalised YREE concentrations in thermal waters from the Mura Basin; a, Le-2g; b, Sob-1, low TDI; c, Sob-1, high TDI; d, T-4 (modified after Kralj, 2004a).

The wells Sob-1 and Sob-2 reached depths of 870.0 m and 855.8 m and tapped Thermal I at 600-646 m and 605-660 m, respectively, as well as some underlying aquifers in the Mura and Lendava Formations. The water belongs to the Na-HCO_3 hydrogeochemical facies, TDI ranges from <1.4 g/L to over 4.3 g/L and averages to 3.2 g/L and 2.5 g/L for the Sob-1 and Sob-2 well, respectively (Table 3). The amount of dissolved CO_2-gas is variable and ranges from some 10 mg/L to over 1,500 mg/L (Kralj, 2001).

Chemical composition of thermal water from the Sob-1 and Sob-2 wells has been varying in time and often considerably deviated from the average (Table 1). In the Sob-1 well, hydrodynamic pressure and temperature in Thermal I have been commonly changing within the time interval of about 70-80 minutes, although during severe over-exploitation conditions, the intervals have been as short as 30-40 minutes. When the pressure in Thermal I increased, the temperature decreased, and vice versa. The maximum recorded difference in pressure and temperature is 0.8 bar and 2.5 °C, respectively. The changes are continuously reoccurring during the well operation, and for that reason, they have been arbitrarily termed well cycling and the time interval of 30-40 and 70-80 minutes a cycle (Kralj, 2004a; Kralj & Kralj 2009; 2012).

Chemical composition of abstracted thermal water varied with the changing temperature and hydrodynamic pressure as well. With the increase in temperature TDI, the amount of dissolved CO_2 and the concentrations of almost all major ions, minor ions/elements and trace elements including YREEs increased in nearly the same manner (Figs. 6, 7), (Kralj & Kralj, 2000a; 2012; Kralj, 2001). When hydrodynamic pressure in Thermal I increased and the temperature decreased, the composition of abstracted thermal water began to change toward lower TDI, lower amount of dissolved CO_2, and lower concentrations of nearly all major ions, minor ions/elements and trace elements. As the abstracted water is a mixture supplied from Thermal I and the underlying aquifers in the Mura and Lendava Formations, the change in hydrodynamic pressure in the aquifers and the change in temperature and chemical composition of water indicates the changing supply from the aquifers.

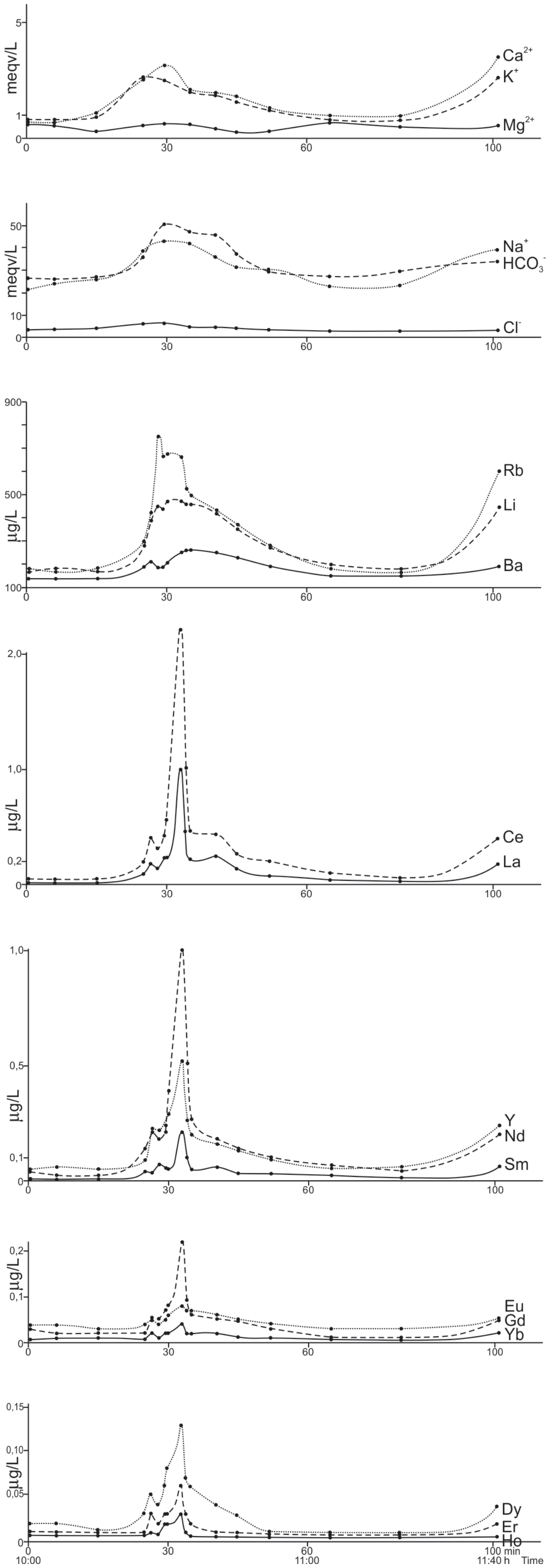

Fig. 6. Temporal variation of concentrations of some major ions, minor ions/elements, trace elements and YREEs in thermal water abstracted from the Sob-1 well on November 11, 1997, from 10:00 h to 11:43 h. The peak of concentrations correlates with the decrease in hydrodynamic pressure in Thermal I (data from Kralj & Kralj, 2000a; 2012).

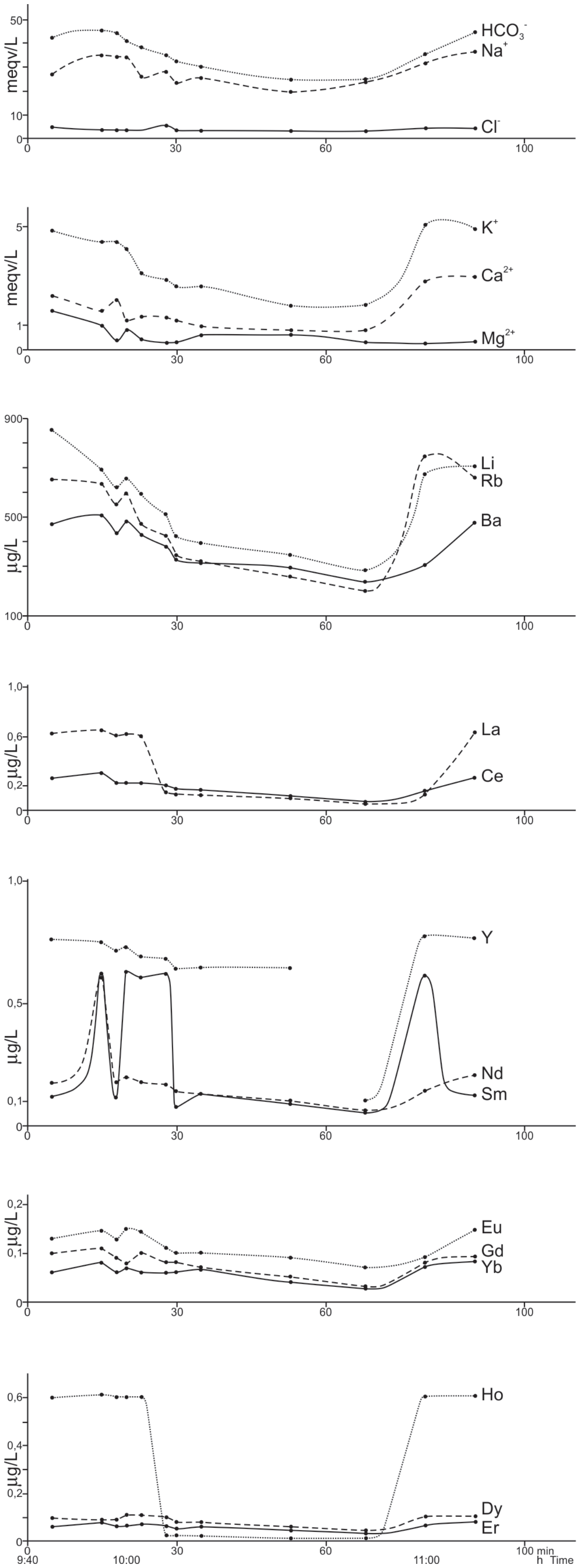

Fig. 7. Temporal variation of concentrations of some major ions, trace elements and YREEs in thermal water abstracted from the Sob-1 well on April 7, 1999, from 09:45 h to 11:10 h (data from Kralj & Kralj, 2000a; 2012).

In thermal water abstracted from the wells Sob-1 and Sob-2, the sum of concentrations of YREEs is, in general, relatively low. For water from Thermal I it amounts to <0.30 µg/L (Table 1; Le-2g and Sob-2, low TDI). The highest sum of 6.23 µg/L has been recorded in water from the Sob-1 well, and the average for the Sob-1 and Sob-2 wells is 2.48 µg/L and 0.84 µg/L, respectively.

The concentrations of YREEs in thermal waters have been normalised to PAAS rather than the aquifer sediment (Table 3). YREE abundances in silty and sandy aquifer sediments from the Sob-1 well-core show some variations (Fig. 3) related to the grain-size and the amount of heavy minerals such as monazite, allanite and xenotime (Ce, Sm, Gd, Dy, Tb), or light minerals, in particular plagioclases (Eu). For that reason, the YREE abundances in the aquifer sediments normalised to PAAS commonly show positive Ce anomaly and positive fractionation of MREEs over HREEs. Yet, the abovementioned heavy minerals have very low solubility in water and therefore unlikely contribute significant amounts of YREEs in thermal water.

The PAAS-normalised YREE concentrations in thermal water from the Le-2g well (Fig. 5) and mixtures of waters from the Sob-1 and Sob-2 wells sourced from or dominated by Thermal I are characterised by fractionation of HREEs and to a lesser extent MREEs over LREEs, with slightly negative Ce and pronounced positive Eu anomalies. In mixed waters from the Sob-1 and Sob-2 wells having higher TDI (Fig. 5), MREEs are positively fractionated over LREEs and HREEs, and the Eu anomaly is moderately positive.

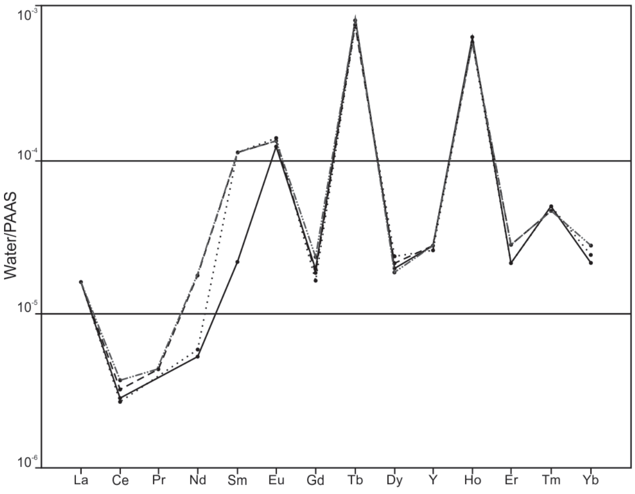

Fig. 8. The plots of PAAS-normalised YREE concentrations in low-TDI thermal water from the Sob-1 well sampled on October 28, 1998 (modified from Kralj & Kralj, 2009). Dotted line – sample taken at 13h 00 min; solid line – sample taken at 13h 35 min; dashed line – sample taken at 13h 45 min.

Similar trends can be seen for temporal variations in chemical composition of abstracted thermal water from the Sob-1 well sampled on October 28, 1998 (Fig. 8) and November 11, 1997 (Fig. 9). On April 7, 1999, the concentrations of YREEs were substantially increased and their PAAS-normalised plots show more pronounced negative Ce anomaly, very high positive Sm and Tb anomalies and very high and moderate positive Ho and Tm anomaly, respectively (Fig. 10).

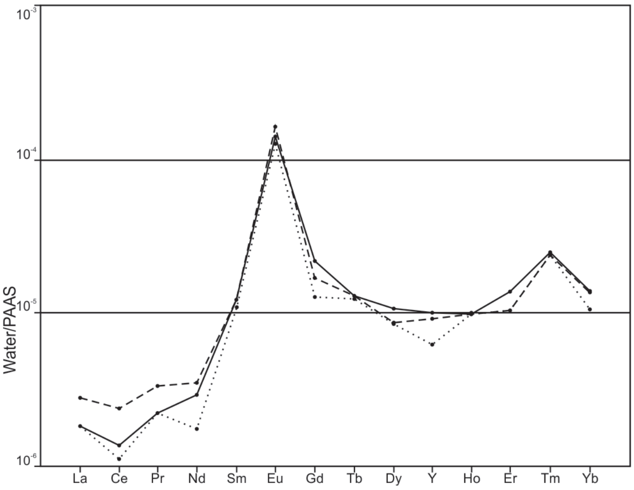

Fig. 9. The plots of PAAS-normalised YREE concentrations in high- (H) and low-TDI (L) thermal water from the Sob-1 well sampled November 11, 1997, from 12:57 h to 13:43 h (data from Kralj & Kralj, 2009). Dotted line – sample taken at 10h 26 min 30 sec; solid line – sample taken at 10h 28 min 45 sec; dashed line – sample taken at 10h 30 min 15 sec; dash--dotted line – sample taken at 10h 32 min 00 sec.

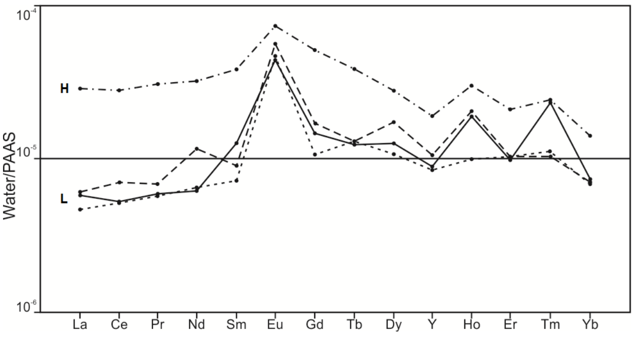

Fig. 10. The plots of PAAS-normalised YREE concentrations in high-TDI thermal water for the Sob-1 well sampled on April 7, 1999 (modified from Kralj & Kralj, 2009). Dashed line – sample taken at 9h 45 min; dash-dotted line – sample taken at 9h 55 min; solid line – sample taken at 9h 58 min; dotted line – sample taken at 10h 00 min.

Discussion

Rare earth elements and yttrium analysed in mineral and thermal waters from Tertiary aquifers in the Mura Basin occur in concentrations far below (10^{-2} to 10^{-4}) the abundances in the aquifer sediments. The original idea of the present study was to identify similarities of the YREE distribution patterns in water and aquifer sediment as they have been reported from various hydrological environments worldwide (e.g., Smedely, 1991; Gosselin et al., 1992; Johannesson & Lyons, 1996; Fee et al., 1992; Möller, 2000; Zhou et al., 2005; Möller et al., 2007). Yet, the normalisation to PAAS seems more convenient. The first reason is mineralogical and geochemical diversity of Tertiary sedimentary successions cold mineral and particularly thermal waters migrated through during their geochemical and thermal evolution. The second reason is carbonate type of waters that influences the solubility and complexation reactions of YREEs and is an important control of their fractionation (Lee & Byrne, 1993; Luo & Byrne, 2004; Guo et al., 2005).

In the areas of cold mineral water springs, Badenian and Sarmatian sediments of the Haloze and Špilje Formations outcrop. Their deeper compartments comprise low-permeability aquifers with waters of diverse hydrogeochemical facies varying inside the composition range of Na-Ca-K-Cl-HCO_3-SO_4 (Kralj & Kralj, 2000a; 2012; Bräuer et al., 2016; Nádor et al., 2012). Deep waters and carbon dioxide ascend toward the surface through fault systems and mix with shallower groundwaters. Owing to the presence of carbon dioxide, the mixed waters undergo further geochemical change related to water-rock interaction. The resulting diverse major ion composition of mineral waters (Table 2) indicates rather individual evolution patterns.

The plots of YREE concentrations in cold mineral waters normalised to PAAS show fractionation of Y and HREEs (YHREEs) over LREEs, and positive Eu anomaly. The observed YHREE/LREE fractionation can be explained by the solubility and complexation of Y and REEs in carbonate waters as they increase with the increasing atomic number or smaller ionic radius (Lee & Byrne, 1993; Luo & Byrne, 2004; Guo et al., 2005). Positive Eu anomalies have been typically encountered in anoxic thermal waters (Michard & Albarède, 1986; Michard et al., 1987; Michard, 1989; Klinkhammer et al., 1994; Douville et al., 1999; 2002) as europium tends to be reduced to more soluble Eu^{2+} state (Sverjensky, 1984; Bilal, 1991), and when in solution, the large Eu^{2+} ion is not easily incorporated in precipitating minerals but commonly remains in solution and/or adsorbed onto mineral surfaces (Möller, 2000).

Low-temperature thermal water (30 °C) from the Haloze and Špilje Formations captured in the well T-4 at Radenci has relatively flat PAAS-normalised YREE pattern with insignificant positive Eu anomaly, although MREEs, Y and HREEs are fractionated over LREEs (Fig. 5). Thermal aquifers in the Haloze and Špilje Formations are characterised by very low permeability, the flow of fluids is slow, and the water-rock interaction times are much longer than in fractured aquifers of mineral waters.

Similar relationship can be recognised for thermal waters captured in the wells Le-2g, Sob-1 and Sob-2. The aquifer Thermal I has relatively well-developed intergranular porosity and good permeability. The plots of PAAS-normalised YREE concentrations in thermal waters captured or sourced from or mainly from Thermal I resemble, in general, those of cold mineral waters showing a distinct positive Eu anomaly and fractionation of MREEs and HREEs over LREEs (Fig. 5). For mixed waters with a higher proportion of waters from the Lendava Formation the YREE PAAS-normalised plots become flatter with a weak positive Eu anomaly and slightly acquired other MREEs, whilst the fractionation of HREEs over LREEs disappears. In the Lendava Formation the aquifers have similar characteristics as in the Haloze and Špilje Formations, carbon dioxide is abundant, the aquifer sediment and water are more equilibrated, and longer times of water-rock interaction enable LREEs to undergo complexation with carbonate ligands and enter the solution the last, after more soluble HREEs and MREEs.

The plots of PAAS-normalised YREE concentrations obtained for thermal waters produced from the Sob-1 well on April 7, 1999 (Fig. 10) differ from those typical for Thermal I or various mixtures with waters from the Lendava Formation. Beside moderate negative Ce anomaly, a pronounced positive Sm, Eu, Tb and Ho anomalies have been recognised. In Table 4, six selected analyses of major ions and trace elements from the cycles sampled on November 11, 1997 and April 7, 1999 are shown. The cycle of April 7, 1999, shows a general increase in the concentration of the potassium ions (K^+), total organic carbon (TOC) and several trace elements, in particular, lithium (Li), boron (B), scandium (Sc), gallium (Ga), selenium (Se), rubidium (Rb), strontium (Sr), caesium (Cs), barium (Ba), thallium (Tl) and YREEs. Chemical composition of thermal water from this cycle and PAAS-normalised YREE concentrations could only be explained by activation of an additional source of thermal water with specific chemical composition and possibly low permeability as it has been recognised as late as during severe overexploitation conditions in the well.

Table 4. Chemical composition of selected samples of thermal water from the Sob-1 well collected on November 11, 1997 (10:00 – 11:43 h) and April 7, 1999, (09:45 – 11:10 h); major ions, dissolved CO_2-gas, dissolved silica (SiO_2), total organic carbon (TOC), total dissolved ions (TDI), pH, temperature of water at well-head (T_{wh}) and trace elements with yttrium and rare earth elements (YREEs).

Sample	**180***	**184***	**190**	**210**	**218**	**221**
Date	11.11. 97	11.11.97	11.11.97	7.4.99	7.4.99	7.4.99
Time	$10^{00'}$	$10^{28'45''}$	$11^{20'}$	$9^{45'}$	$10^{33'}$	$11^{10'}$
Ions (mg/L)						
Na^+	490	990	530	620	450	820
K^+	32	98	33	190	70	190
Ca^{2+}	14	63	21	43	15	57
Mg^{2+}	8	6	5	19	5	3
HCO_3^-	1600	3100	1830	2600	1500	2700
Cl^-	120	220	91	159	95	124
F^-	0.45	0.92	0.73	0.47	0.45	0.62
J^-	0.05	0.07	0.04	0.15	0.10	0.19
Br^-	0.41	0.64	0.36	0.60	0.45	0.77
SO_4^{2-}	8	51	8	75	12	48
TDI	2,273	4,530	2,519	3,708	2,148	3,944
Oxides/Dissolved gas						
SiO_2 (µg/L)	18	17	18	13	14	24
CO_2 (mg/L)	546	744	637	575	440	712
Parameters						
TOC (mg/L)	1.2	1.9	1.4	2.3	2.5	12.1
T_{wh} (°C)	48.4	48.7	48.7	48.8	48.6	48.9
pH	6.44	6.67	6.49	6.69	6.81	6.86
Trace elements (µg/L)						
Li	170	440	180	854	343	700
Be	0.2	1.1	0.3	1.5	0.7	1.3
B	559	1480	678	4000	1100	2800
Al	31	22	17	28	19	75
Sc	1.8	2.2	1.9	7.1	7.6	7.1
Ga	0.09	0.12	0.10	0.62	0.64	0.62
As	2.7	2.9	2.3	3.0	3.8	3.1
Se	2.1	4.8	1.3	6.5	4.4	7.1
Rb	181	668	166	654	258	656
Sr	775	969	827	1470	982	1530
Y	0.05	0.24	0.06	0.76	0.64	0.76
Zr	0.1	0.3	0.1	1.3	0.4	1.0
Cs	6.1	26.8	6.3	34.4	13.2	32.3
Ba	140	190	150	477	292	477
La	0.02	0.24	0.03	0.63	0.09	0.63
Ce	0.05	0.42	0.06	0.26	0.11	0.25
Pr	<0.01	0.05	<0.01	0.04	0.02	0.04
Nd	0.04	0.21	0.04	0.18	0.10	0.20
Sm	<0.01	0.07	0.01	0.12	0.09	0.12
Eu	0.04	0.05	0.03	0.13	0.09	0.14
Gd	0.03	0.07	0.01	0.10	0.05	0.09
Tb	<0.01	0.01	0.01	0.61	0.60	0.61
Dy	0.02	0.06	0.01	0.10	0.06	0.10
Ho	<0.01	0.02	<0.01	0.60	0.01	0.60
Er	<0.01	0.03	<0.01	0.06	0.04	0.08
Tm	<0.01	0.01	<0.01	0.02	0.02	0.02
Yb	<0.01	0.02	<0.01	0.06	0.04	0.08
Tl	0.17	0.37	0.11	0.86	0.62	0.79

*data from Kralj & Kralj, 2009

The increased concentrations of the K^+ ions and Li, B, Rb, Ba and Cs in the water from the assumed additional source indicate a possible origin in dissolution of illite and muscovite, which are the principal phyllosilicate minerals of the aquifer sediments in the Sob-1 well (Žlebnik et al., 1988a; Kralj, 2001). Illite contains trace amounts of YREEs and its decomposition could also be the source of YREEs and their fractionation. Many studies carried out worldwide have shown that during water-rock interaction LREEs are retained at the site of reaction by adsorption to residual phases while YHREEs are preferentially mobilized by solution complexation reactions (e.g., Duddy, 1980; Braun et al., 1993; Johannesson and Zhou, 1999; Zhou et al., 2005). Guo et al. (2005) have shown for carbonate waters that there is a steady increasing trend of REE solubility according to atomic number or decreasing ionic radii for (+3) ions, except for Sm and Ho, and to a lesser extent Tb that show relatively higher solubilities. The observed PAAS-normalised pattern in the waters from the cycle of April 7, 1999, could be explained by the process of decomposition of illite and muscovite, and preferential mobilisation of HREEs into solution.

On the other hand, the increased concentrations of TOC, gallium, selenium, thallium and the iodide ions I^- also indicate the assumed additional (or another additional) source. This group of elements could have an origin in waters leaked from silty and clayey layers rich in organic matter and coal, that have been activated only during severe overexploitation conditions. In that case the ligands complexing YHREEs could be, beside carbonate species, humic and/or fulvic acids.

Conclusions

Rare earth elements and yttrium analysed in mineral and thermal waters from Tertiary aquifers in the Mura Basin occur in concentrations that are far below (10^{-2} to 10^{-4}) the abundances in the aquifer sediments. Mineral and thermal waters are carbonate waters, and the concentrations of YREEs and their PAAS-normalised patterns strongly depend on the YREE solubility, complexation reactions and the duration of water-rock interaction. In aquifers with moderate to high permeability and high flow rates YREE concentrations in water indicate lower degree of equilibration with the aquifer sediment. The plots of YREE concentrations normalised to PAAS show fractionation of YHREEs over LREEs which could be attributed to the higher solubility of YHREEs and their preferential mobilisation into solution by complexation reactions. In low-permeability aquifers the retention times and water-sediment interactions are longer and equilibration reactions more advanced as the fractionation of YHREEs over LREEs disappears. The same trend has been recognised for the positive Eu anomaly which is outstanding in cold mineral waters and thermal waters from Thermal I, and weak in the waters from low-permeability aquifers in the Haloze, Špilje and Lendava Formations.

In the Sob-1, uncommonly high concentrations of YREEs and their specific PAAS-normalised plots indicate the well overexploitation and the consequent leakage from low-permeability clayey and silty lenses rich in organic matter and coal. Here, the YHREE complexing ligands could be, beside carbonate species, humic and/or fulvic acids.

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