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The influence of tectonic setting on groundwater chemical composition in the Peshkopi gypsum karst area, Korab Mountains, Eastern Albania

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The diversity of groundwater chemistry in the Peshkopi gypsum karst area may be related to its setting within the tectonically active Korab Massif (Albania), as shown by field tests of temperature, pH, Eh and EC, and sampling of the waters for chemical analysis (both major and trace components) from cool brackish springs and mineralized thermal springs. The relationship between the chemical composition of the spring waters and of the reservoir rocks was elucidated by analysis of anhydrite-gypsum rocks and experimental dissolution of an anhydrite-gypsum sample. Statistical analysis was used in the processing of hydrochemical data. Comparison of analytical results from 2019 with earlier data indicates compositional stability of the groundwaters over time. Our results together with statistical analysis of the hydrochemical data support an earlier hypothesis of two systems of groundwater circulation within the anhydrite-gypsum deposits of the Peshkopi region. A shallow circulation system involves cold (10–14°C), mainly brackish SO_4-Ca waters with very low concentrations of Na^+ and Cl^- ions, reflecting their formation in a sulphate rock environment that probably corresponds spatially with a gypsum layer formed by hydration of anhydrite in the near-surface zone. A deep circulation system conditioned, *inter alia*, by the presence of a large fault, brings to the surface water at up to 44°C, saturated with H_2S, mineralized, of the SO_4-Ca type with an increased content of Na, K, HCO_3, Cl, BO_3 and SiO_2. The chemical composition of these waters, regardless of the presence of large amounts of sulphates, is significantly different and suggests the influence of other factors on their formation, such as slow circulation, contact with flysch rocks in the fault zone and the mixing of deep and near-surface waters in the final part of their ascent to the surface.

Key words: gypsum karst, groundwater shallow and deep circulation systems, water chemical composition, thermal springs, Albania.

INTRODUCTION

Karst waters are related to soluble rocks such as carbonate, mainly limestone and dolomite, and evaporites, mainly gypsum and anhydrite. At a global scale ~15.2% of the ice-free continental surface consist of rocks with karst-forming potential, while in Europe it is 21.8% (Chen et al., 2017; Goldscheider et al., 2020). Evaporite rocks such as gypsum, anhydrite and salt occur beneath 25% of the continental surface (Ford and Williams, 2007). Karst in evaporite rocks occurs in a wide number of regions of the world. In Europe, the largest areas of gypsum karst are within the East European Plain (Klimchouk and Andreychouk, 1996; Klimchouk et al., 1996), but in most countries their outcrop is small, as in Spain 7% (Gutiérrez et al., 2008), and in Italy 1% (Chiesi et al., 2010; De Waele et al., 2017).

The karst landscapes in Albania cover 6750 km^2, or ~24% of the country's territory, which are represented mainly of carbonate rocks. Evaporite rocks cover 260 km^2, comprising ~1.7% of the Albanian territory (Melo et al., 1991; Eftimi, 2010, 2020). They form two evaporite karst areas, Korab (Peshkopi) and Dumre, representing evaporite domes (Fig. 1). Both areas are characterized by specific geologic, tectonic, and geomorphological conditions resulting in different hydrogeological characteristics.

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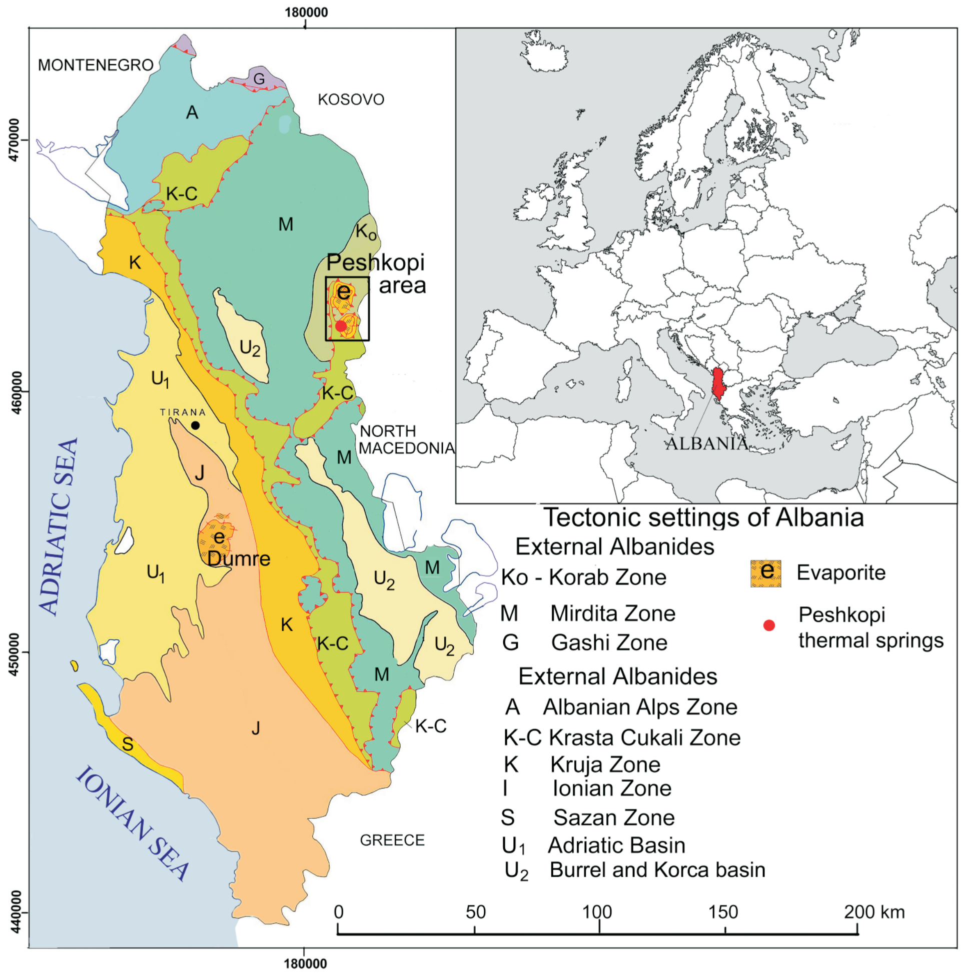

Fig. 1. Tectonic divisions of Albania (after Xhomo et al., 2002) and location of the Peshkopi area

The Peshkopi area, the area of study, is well known for its thermal springs (Avgustinski et al.,1957; Safanda et al., 2004; Eftimi and Frashëri, 2016), which are a hydrogeological phenomenon of both scientific and practical importance.

Here we analyse the diversity of groundwater chemistry in the Peshkopi gypsum karst area and explain the basic factors (rock lithology and tectonic conditions) determining the chemical composition of the water. For this purpose, field tests of temperature, pH, Eh and electrical conductivity were carried out in October 2009 and May 2019 and water samples were taken for chemical analysis (including major and trace components) from brackish springs and mineralized thermal springs. In order to examine the relationship between the chemical composition of the springs and the composition of the reservoir rocks, anhydrite-gypsum rocks (3 samples) were analysed and experiment dissolution of an anhydrite-gypsum sample in distilled water was carried out. Statistical analysis was an important methodological tool used in the processing of the hydrochemical data.

STUDY AREA

The Peshkopi thermal area is in the central part of the Korab Tectonic Zone (Fig. 1), at the boundary with North Macedonia, and consists mostly of Mt. Korab which, with its numerous peaks more than 2000 m above sea level, serves also as a drainage divide between Albania and North Macedonia. The highest peak, called Mt. Korab, is 2751 m a.s.l., the highest in Albania (Fig. 2). Steep and fast-flowing mountain creeks and rivers form deep V-shaped gorges, locally of canyon-like shape, intensively eroding Mt. Korab in the west.

The most important rivers in the study area are the Banja River that crosses the southern gypsum outcrop, while the Gypsum and Veleshica rivers cross the north gypsum outcrop (Fig. 2). All three rivers join the Drin River that flows through the central part of the Peshkopi intermontane depression. Their wide valleys are locally filled with thick and coarse clastic deposits.

Albania is part of the Mediterranean Alpine Fold Belt and belongs to Dinaric-Hellenic range. The geological structure of the Albanides comprises two major units: the Internal Albanides to the east and the External Albanides to the west (Fig. 1; Meço and Aliaj, 2000). Structurally, the Peshkopi area represents the west limb of the great Korab anticline, which is part of the Korab tectonic zone (Fig. 1). This tectonic zone consists mainly of Paleozoic terrigenous metamorphic rocks and is characterised by compressional tectonic forces (Aliaj, 1992, 2012). The core of the structure consists of slates, effusive and carbonate metamorphic rocks of Silurian-Devonian age, which continue with sandstone and conglomerate of Permian to Lower Triassic age. These are overthrusted by Paleogene and Cretaceous flysch followed by Upper Cretaceous limestone of the Krasta zone (Fig.1). The highest peak, that of Mt. Korab, consists of stratified limestone and marble of Silurian-Devonian age.

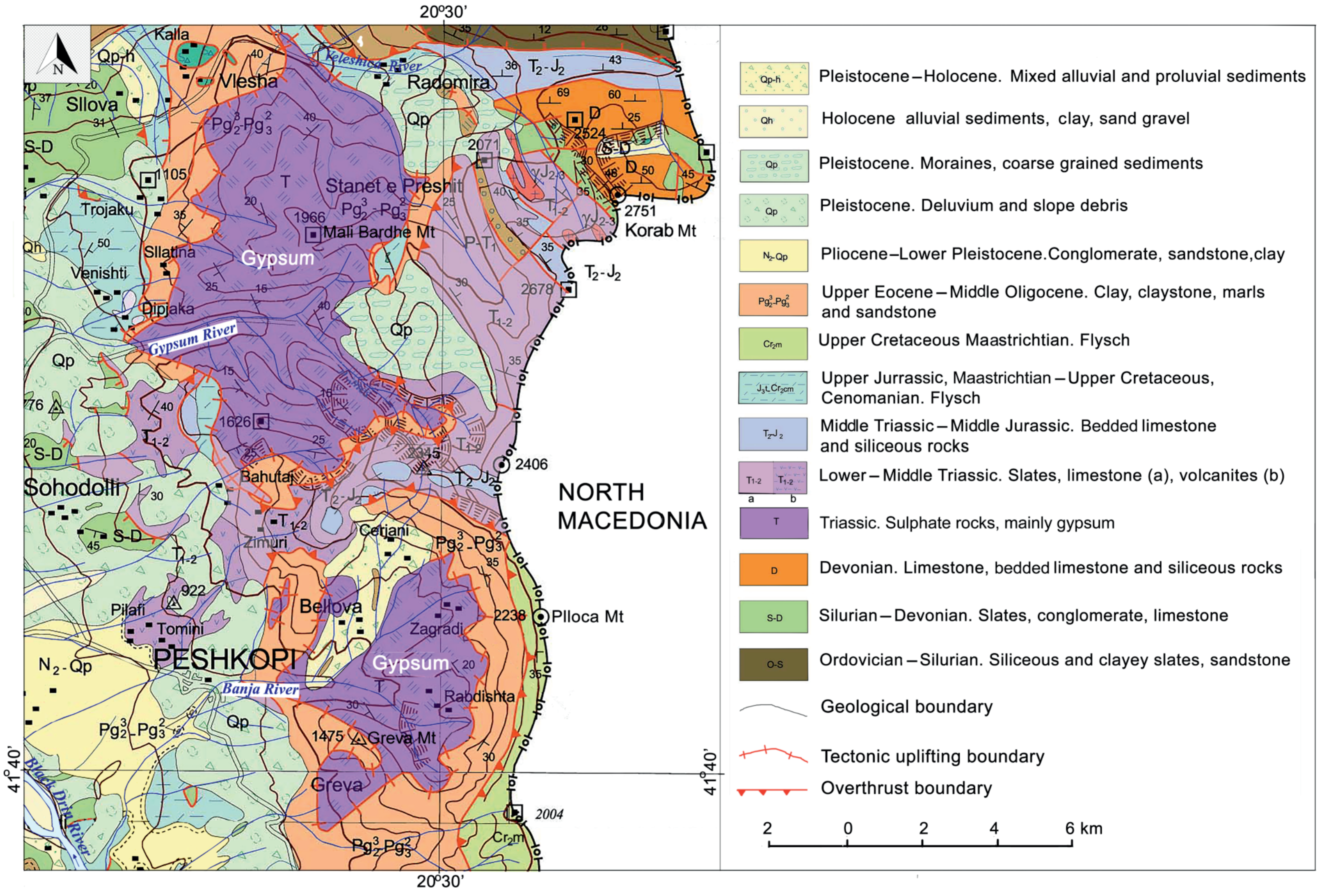

Fig. 2. Geological map of the Mt. Korab area (after the 1:200,000 geological map of Albania)

The most important geological characteristics of the Korab area comprise two gypsum tectonic windows representing diapirs, which have created cupola structures. The southern gypsum dome covers ~24 km^2, and the northern outcrop ~66 km^2 (Fig. 1). On the Geological Map of Albania at 1:200,000 scale the age of the gypsum deposits is shown as Triassic (Xhomo et al., 2002) but there are also suggestions of an older age (Xhomo et al., 1991; Aliaj, 1992).

The Korab Zone was affected by a strong extensional regime during the Pliocene-Quaternary, which resulted in the establishment of horst-graben structures (Aliaj, 1998). The graben developed along the Black Drin River fault zone is expressed topographically by a vertical amplitude of over 1200 m. Thermal springs near Peshkopi issue along this fault zone (Aliaj, 1998; Arsovski, 1974). Evaporite tectonics influenced the development of regional thrust faulting and are first order controls on the formation of the thermal water, as described by Velaj (2002). The rise of Mount Korab facilitated erosion, and the accumulation of thick coarse clastic deposits, which fill the wide valleys of the Gypsum and Banja rivers, of thickness in places of ~15 m.

The gypsum rocks are mainly massive, though partly form near-horizontal or gently westwards dipping strata. The central parts of the gypsum include anhydrite crystals, showing that initially the rock has been anhydrite, which then later transformed into gypsum. The transformation of anhydrite into gypsum occurs with an increase in volume (“swelling”) of the rock of between 30 and 58% in the near-surface zone where circulating water encounters the anhydrite (Yilmaz, 2001). Calcite veins are also present in the gypsum rocks. Chiesi et al. (2010) described the transformation of anhydrite into gypsum associated with karstification of the near-surface gypsum zone, a process similar to that developed in the anhydrite-gypsum outcrops of the Peshkopi area of Mt. Korab.

The sulphate massif is mainly composed of finely layered (Fig. 3A) and massive anhydrite (Fig. 3B), which have largely hydrated and continue to hydrate. Hydration processes are favoured by the geomorphological location of the massif on the valley slope, significant sealing (fracturing) of the anhydrite, plastic deformation of the strata, and high precipitation (>1,000 mm per year).

At the foot of the Gypsum and Banja river banks, caves 1 to 5 m long are often developed, where small or temporary springs may issue (Fig. 4A, B). The karst well cavities are rare but Figure 4C shows a well clogged by thick deposits of residual material and detritus, discovered on Mt. Bardhe (Bassi et al., 1999). The sinkholes, mostly developed at high elevations on Mt. Bardhe, usually have a diameter of ~1-4 m and a depth up to 2 m. When the sinkholes join each other, they form karst “valleys” (dolines) up to 80 m in length; the most attractive of these is located at the top of an erosional block (tower karst), in the upper part of the Banja River (Fig. 4D).

The climate of the area is cold Mediterranean mountainous (Jaho et al., 1975); in the town of Peshkopi, at elevation ~650 m a.s.l., the mean annual temperature is 11°C; in January it is –0.2°C and in August 26.6°C. The average rainfall is ~920 mm and is unevenly distributed throughout the year; ~70% of rainfall occurs from October to March. In the mountain area, which is much higher than the town of Peshkopi, the average annual temperature and rainfall are respectively ~8°C and ~1,200 mm.

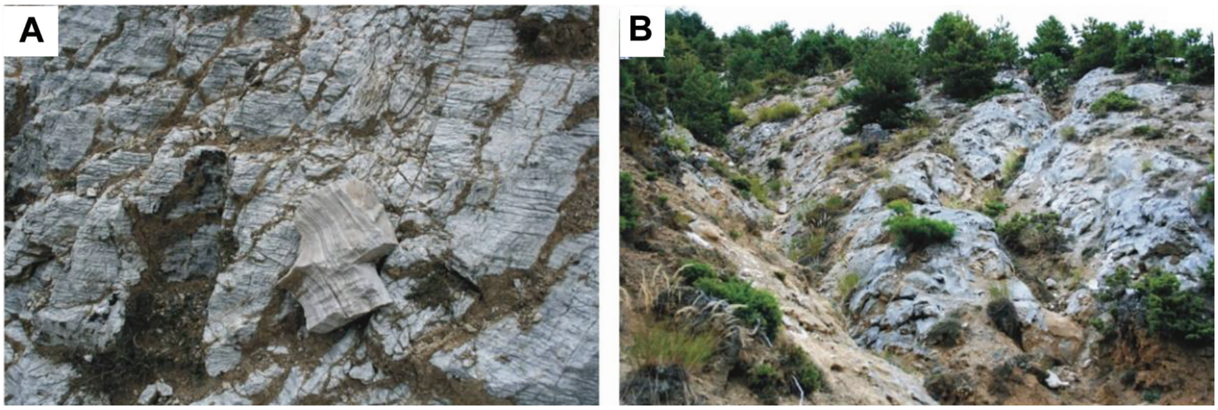

Fig. 3. Anhydrite rocks: finely layered (A) and massive (B)

A – finely-layered character of anhydrite rock; **B** – exposure of anhydrite on a valley slope (photos by V. Andreychouk)

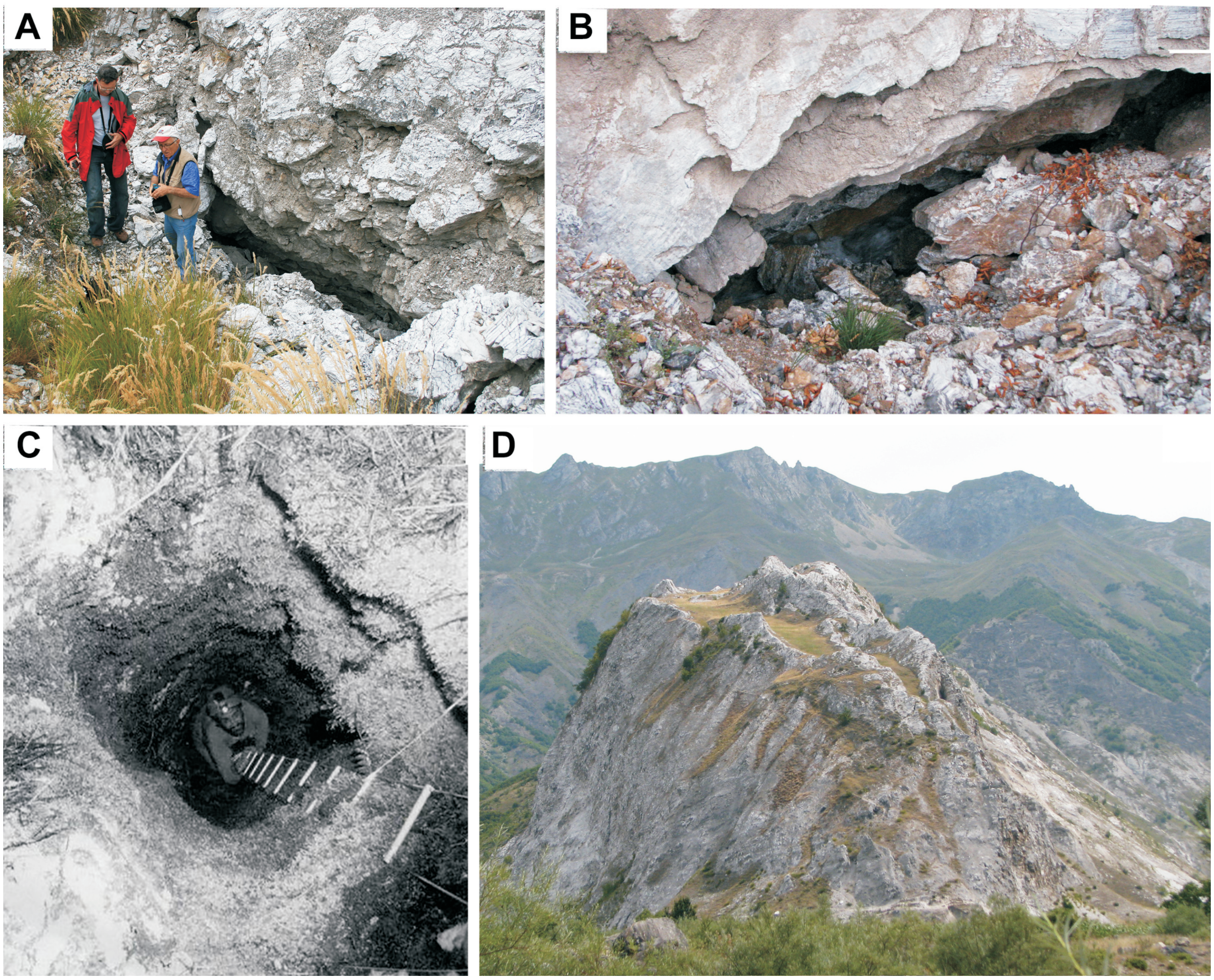

Fig. 4. Gypsum outcrops and some karst landforms

A – gypsum river bank; **B** – on Banja River bank; **C** – exploration of a natural well on Mt. Bardhe (photo by G.S. Faentino); **D** – solution dolines at the top of a karst erosional gypsum block in the upper part of the Banja River (photos by V. Andreychouk – A and B and R. Eftimi – C and D)

MATERIALS AND METHODS

For analysis of the hydrogeological characteristics of the study area, the data used included geological (Xhomo et al., 2002) and hydrogeological maps (Eftimi et al., 1985), and some publications on the Peshkopi thermal springs (Avgustinski et al., 1957; Jóźwiak et al., 2012; Eftimi and Frashëri, 2016, 2018), together with other data. Most of these sources represent archive materials such as reports, chemical analyses, and historical monitoring of the Albanian Hydrogeological Service (AHS). The archived data was compared to recent field observations. The authors carried out hydrochemical analyses of the springs in October 2009 and May 2019. In the field, water temperature, EC, pH and Eh were tested. Water samples were collected in plastic 0.5 l containers, transported, and stored at low temperature (2–7°C) until analysis. All samples were filtered through a standard membrane filter (pore size 0.45 μm). Filtered samples were placed into two polyethylene containers. The samples destined for cation analyses were acidified with nitric acid down to pH <2.

The chemical composition of the water, including macro- and microelements, was determined at the Hydrogeochemical Laboratory of the Faculty of Geology, Geophysics and Environmental Protection of the AGH University of Science and Technology in Kraków (Poland). The analyses were made by an ICP-MS (inductively coupled plasma ionisation mass spectrometer) model *iCAP RQ (C2)* from *Thermo Scientific* and ICP-OES (optical emission spectrometer with excitation in inductively coupled plasma) model *Optima 7300DV* from *Perkin Elmer*.

For investigation of the relation between the chemical composition of the rocks and that of the groundwater, three samples of sulphate rocks, mostly of anhydrite, were taken. Geochemical studies of the samples were performed at the Geochemical Laboratory of the Academia Bialska in Biała Podlaska (Poland). In addition, dissolution of a sample of anhydrite-gypsum (typical of the study area) in distilled water was performed over the period 29.10–22.11.2021 at the Water Analysis Laboratory of the Institute of Earth Sciences of the University of Silesia in Katowice (Poland).The Acquachem program was used to develop water chemistry data.

Processing of hydrochemical data included statistical analysis. The hydrochemical data of all tested waters were compared with that of an experimental sample, the composition of which reflects the chemical composition formed solely by the interaction of sulphate rock with water. According to our hypothesis, the degree of similarity between the composition of the test water sample and the composition of the experimental sample can indicate the extent to which the chemical composition of the waters is determined by dissolution of the sulphate rock. A lower similarity or a complete lack of correlation indicates the decisive influence of other factors. In this way, we can identify waters whose composition is shaped solely by the shallow circulation system, and waters whose composition is determined largely by other factors present in the deeper water circulation system.

RESULTS

GROUNDWATER: CIRCULATION AND CHEMICAL COMPOSITION

From the hydrogeological point of view, the rocks of Mt. Korab are characterised by the presence of two rock types of different permeability: highly permeable karst rocks outcropping mainly in the central part of the mountain, these being surrounded by low-permeability to practically impermeable rocks (Figs. 5 and 6). The impermeable rocks consist of different rock types as regards their age and lithology, and include metamorphosed Paleozoic and Triassic rocks such as slate and marble, and Eocene flysch deposits (Fig. 5).

The high-permeability rocks consist of limestone and gypsum. The Korab peak comprises (Fig. 2) stratified limestone, together with schist, sandy conglomerate, volcanic rocks, and marble. Although the limestone has a relatively small outcrop, it contains important fresh karst water resources. Two large karst springs issue from the limestones of Mt. Korab, the discharge of which varies from ~100-150 to >400 l/s. One (the Radomira spring) is used for the water supply of the town of Peshkopi (Fig. 5).

The groundwater in the gypsum was studied. The northern gypsum outcrop is drained by the Gypsum River and the southern one by the Banja River. Both outcrops are characterized by an striking combination of two landscapes: erosional and karstic.

In the Peshkopi gypsum-dominated evaporite outcrops, dehydration has facilitated the creation of two karst circulation systems with very different physico-chemical qualities (Eftimi and Frashëri, 2016): a shallow system (within the gypsum cover) and one within the anhydrite extending deep into the rocks following a network of fissures and faults. This general picture is characteristic of areas where gypsum prevails over anhydrite, facilitating the development of a deep groundwater circulation system (Chiesi et al., 2010).

The water in the gypsum mostly circulates at shallow depths along fissures created by the dehydration of the gypsum, whereas the thermal springs are recharged by ascending deep fluids circulating along a deep fault (Fig. 6). The Banja thermal springs near Peshkopi issue at lower elevation along the margins of the gypsum outcrop, as observed also in other gypsum areas (Calaforra and Pulido Bosch, 1993; Omelon et al., 2006).

Table 1 shows the results of chemical analyses of cold brackish and thermal springs, and photos of springs are shown in Figure 7.

COLD GYPSUM SPRINGS

The springs recharged by the shallow karst circulating system are permanent or temporary cold brackish springs. The largest of these emerge mainly along the deep valleys of the Gypsum and Banja rivers (Figs. 5 and 7). Important groundwater resources are drained also in thick clastic deposits filling the riverbed. Consequently, the mean discharge of the Gypsum River, during the dry season, is ~200-300 l/s, while that of the Banja River is ~100-150 l/s. The most important springs, of Brezhdan and Konri, emerge in the Banja River valley (Figs. 5 and 7). Their discharges vary from ~100 to ~250 l/s.

Cold springs of the Korab massive gypsum are characterised by temperatures around 10–14°C. Their water has low contents of Cl^- and Na^+ ions which indicates that the gypsum does not contain salts as in the case of the Dumre gypsum plateau in Central Albania (Andreychouk et al., 2021; Eftimi et al., 2022). The shallow circulating spring water is in equilibrium with the gypsum deposits. The springs are saturated or close to calcium saturation (Jóźwiak et al., 2012).

Waters representing the shallow circulation system are characterised by a weakly acidic to weakly alkaline pH (6.89–7.80). These waters are mineralised (TDS 1547–2515 mg/l; EC 1695–2310 μS/cm), very hard (TH 1176.9–1868.9 mg $CaCO_3$/l), with non-carbonate hardness predominant (21.23–34.56 mval/l). The redox potential corresponds to conditions ranging from oxidising to transitional, at the boundary between oxidising and reducing (Eh 156–202 mV). Major ion concentrations fall within rel-

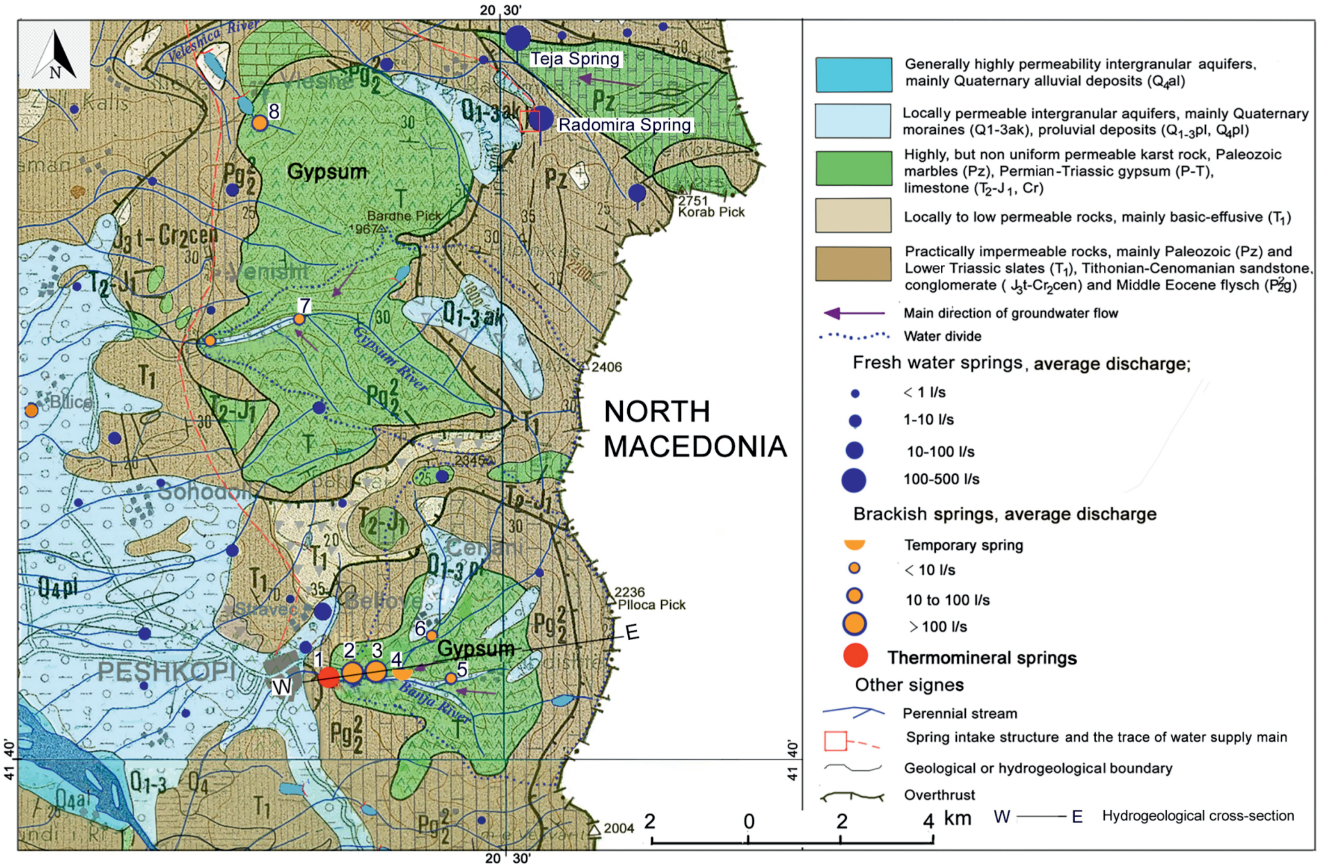

Fig. 5. Hydrogeological map of the Peshkopi area (after Eftimi et al., 1985)

Springs: **1** – Banja (thermomineral spring); **2** – Brezhdan; **3** – Konri; **4** – gypsum spring (temporary); **5** – Rabdishta; **6** – Bellova; **7** – Gypsum River; **8** – Vlesha

atively wide ranges: Ca 436–704; Mg 6.4–37.2; Na 1.13–5.25; K 0.1–0,99; HCO_3 116–172; SO_4 998–16214; Cl 4.5–5.7 (mg/l). According to the Shchukariev's classification, they represent the SO_4-Ca type. In the waters of the Brezhdan spring, slight anthropogenic water pollution was found (or the springs circulate relatively deeper), manifested in higher concentrations for: Na 26.55; K 4.45; Cl 32.0 (mg/l) (Table 1).

The Brezhdan spring issues at a lower elevation (Table 1) than the other cold springs and has a relatively higher temperature and TDS, respectively ~2°C and ~1000 mg/l. The groundwater recharging the Brezhdan spring seems to circulate relatively deeper than the groundwater flow recharging the other cold springs. To better understand the formation of the cold brackish springs of the study area, a sulphate rock dissolution experiment was performed.

The cold gypsum springs of the Peshkopi area are exclusively fed by the infiltration of meteoric waters. No allogenic losses of surface waters in gypsum deposits have been recorded, so under these circumstances, the recharge in the area is fully autogenic.

SULPHATE ROCK DISSOLUTION EXPERIMENT (IN COLD CONDITIONS)

Analysis of the elemental composition of the three samples taken showed the following distribution of components (data rounded in ppm): Ca (207660–213562), S (95867–207933), Sr (1473–1802), Mn (156–60107), Al (35–475), Fe (25–465), Na (29–450), Li (8.6–160.6), Ni (5.1–6.8), K (0.001–785), Mg (1.1–8.8), Ce (1.2–2.0), Tm (0.184–0.566). In trace amounts there are: Dy (<0.001–0.566), Rb (<0.048), Bi (<0.009), Pb (<0.004), Th (<0.003), Pr (<0.003), Sm (<0.002), Tb (<0.002), U (<0.0013). The content of other (analysed) elements, such as Ba, Cd, Co, Cr, Cu, Eu, Er, Gd, Ga, Ho, La, Nd, P, Se, V, Y, Yb, Zn, As, Ti and Mo is <0.001 ppm.

In order to study the chemical variation of the different spring waters draining the shallow or deeper circulation systems, an experiment was conducted to dissolve a typical sample of anhydrite-gypsum in distilled water[1]. The sample was taken around one of the karst springs from the undisturbed rock after it had been thoroughly cleaned of its weathered cover. The experiment was conducted over 29.10–22.11.2021. The 13.9 g/l sample was crushed and placed in a 1l PVC bottle, which was then filled with distilled water. The water sample was shaken regularly, every 2–3 days. EC tests were performed to observe the dynamics of the dissolution process of the rock sample in water, with the following results: 04.11.2021. EC = 2119 μS/cm (in temp. 22.1°C); 09.11.2021. EC = 2230 μS/cm (in temp. 20.3°C); 17.11.2021. EC = 2230 μS/cm (in temp. 20.0°C); 22.11.2021. EC = 2240 μS/cm (in temp. 21.7°C; pH = 7.66; Eh = 176 mV). The experiment was concluded when the mineralisation of the aqueous solution reached a value close to that of the water sampled from the springs. The physical and chemical properties and chemical composition of water are shown in Table 1.

[1] We consider this acceptable, since the mineralization of both kinds of rainwater, infiltrating into the sulphate massifs and surface water and runoff from the higher parts of the Korab Mountains (meltwater and water in contact with metamorphic rocks) is very low

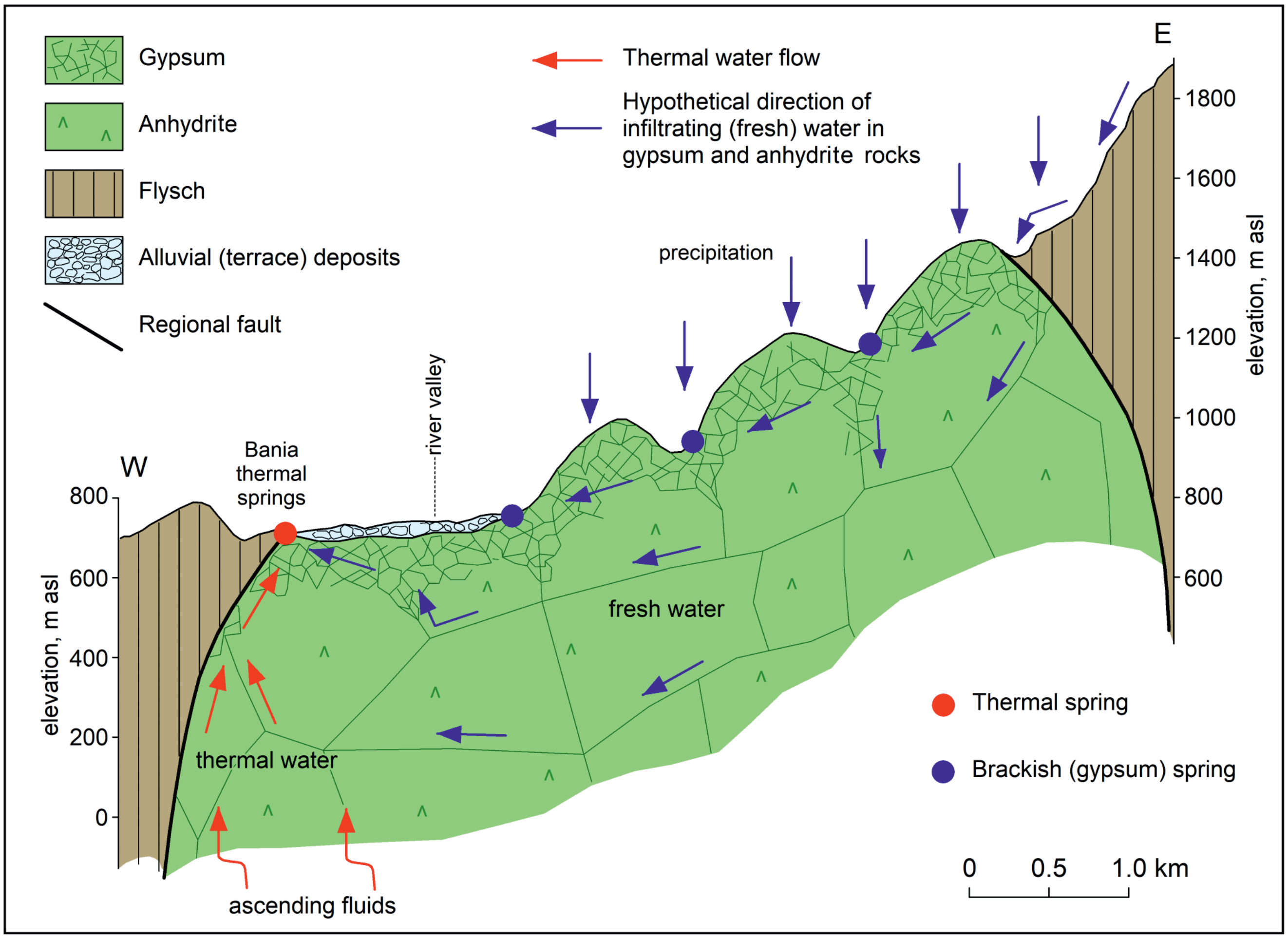

Fig. 6. Hypothetic scheme of groundwater circulation in the Peshkopi area (after Eftimi and Frashëri, 2016); cross-section location is shown on Figure 5

THERMAL GYPSUM SPRINGS

The Korab area includes two important sulphur thermo-mineral springs known as the Peshkopi Spa, issuing in the western periphery of the Banja River gypsum outcrop. The springs issue just along the fault contact line of the gypsum deposits with the impermeable Paleogene flysch deposits (Figs. 5 and 6). The formation of the springs is related to the deep fault developed along the Black Drin River (Melo, 1966; Melo et al., 1991; Xhomo et al., 2002). Along this, the hot waters extend deep into the rocks following a network of fractures and fissures, usually where gypsum prevails over anhydrite (Chiesi et al. 2010).

Waters representing the deeper circulation system are characterised by temperatures of ~35°C to 43.5°C, a total H_2S content of ~50 mg/l, and are weakly acidic (pH 6.20–6.40); the upward flow of the springs is ~23 l/s (Table 1). These are waters with much higher mineralisation (TDS 4068.3–4185.1 mg/l; EC 4500–4600 μS/cm), very hard (TH 2225–2307 mg $CaCO_3$/l), with non-carbonate hardness as predominant (32.60–36.03 mval/l).

The redox potential of the waters was for Banja spring (1) 39 mV, for Banja spring (2) 240 mv, which corresponds to conditions of weakly acidic pH, reducing and at the boundary between oxidising and reducing. Major ion concentrations range from: Ca 744–768; Mg 89–95; Na 254–267; K 46–48; HCO_3 616–726; SO_4 1666–1833; Cl 436–445; BO_3 26–28 (mg/). According to Shchukariev's classification, they are of different types than the waters of the shallow circulation system: SO_4-Cl-HCO_3-Ca and SO_4-Cl-Ca (Table 1).

The average geothermal gradient for the Peshkopi area is ~20°C/km and surface heat flow 76 mW/m^2 (Safanda et al. 2004). The Peshkopi area has a lower mean geothermal potential compared to other Balkan countries such as Croatia (Borović et al., 2016) and Greece (Lambrakis and Kallergis, 2005).

TEMPORAL STABILITY OF THE CHEMICAL COMPOSITION OF THE THERMAL SPRINGS

The temporal stability of the chemical composition of the Peshkopi thermal springs was established by comparison between the results of chemical analyses performed during 1954 (Avgustinski et al., 1957), and the analysis performed during this study in 2019 (Table 1). The differences in the ion concentrations between the old and new analyses is mostly less than 10%; the largest discrepancy is of Na^+, of nearly 20% only in thermal spring 1. This pattern of chemical stability of the Peshkopi thermal spring over the period studied is consistent with other studies of thermal waters extended to periods >100 years (Franko and Melioris, 1999; Dušan et al., 2010). These have established also that the chemical stability is higher for the thermal waters circulating in older rocks, as is the case of the Peshkopi thermal water circulating in Permian-Triassic deposits.

Table 1

Hydrochemical parameter concentrations of springs in the Peshkopi area

Parameter, component	Units	Thermal springs				Cold brackish springs						Gypsum dissolution[1]
		Banja 1	Banja 1	Banja 2	Banja 2	Brezhdan	Konri	Gypsum River	Rabdisht	Belova	Vlesha	
Data		1955	2019	1955	2019	2019	2019	2019	2019	2019	2019	2021
Elevation	m asl	688	688	688	688	715	746	830	935	950	880	
Discharge	l/s	14	14	8	8	100–300	70–250	0–250	1–9	1–12	4–80	
Temperature	(°C)	43.5	43.5	35	35	12.2–13.3	10.7–12	9.7–12.5	?	?	?	
pH	–	6.5	6.40	6.4	6.20	6.89	7.45	7.51	7.54	7.80	7.52	7.40
Eh	mV	–	39	–	240	202	179	172	156	163	173	179
Total dissolved solids (TDS)	mg/l	4050	4068.3	3530	4185.1	2515.1	2408.7	1595.1	1546.7	2231.7	2376.2	2034.1
Total hardness (TH)	mg $CaCO_3$/l		2224.9		2306.8	1868.9	1772.4	1227.9	1176.9	1657.1	1783.5	1433.5
EC (25)	µS/cm	–	4500	–	4600	2310	2120	1935	1695	2160	2110	2240
H_2S–total	mg/l	49.5		32.8								
H_2SiO_3	mg/l		70.91		75.43	12.35	8.58	6.50	5.85	6.37	5.07	<0.26
SiO_2	mg/l		54.54		58.02	9.50	6.60	5.00	4.50	4.90	3.90	<0.20
Cations:												
Na^+	mg/l	279.2	254.4	220.0	267.0	26.55	4.74	5.25	4.10	5.18	1.13	<0.10
K^+	mg/l	53.7	45.80	46.1	48.44	4.45	0.97	0.96	0.63	0.99	0.10	<0.20
Li^+	mg/l		0.958		1.021	0.093	0.007	0.008	0.007	0.007	0.003	<0.005
Ca^{2+}	mg/l	825.7	743.9	753.5	767.8	687.8	659.6	451.9	435.7	639.8	704.2	573.5
Mg^{2+}	mg/l	99.6	89.63	83.0	95.03	37.15	30.79	24.40	21.83	14.78	6.44	0.62
Ba^{2+}	mg/l		0.03		0.01	0.025	0.013	0.015	0.012	0.016	0.016	0.007
Sr^{2+}	mg/l		8.5		8.8	5.093	4.555	3.973	3.412	3.893	4.665	6.57
Mn^{2+}	mg/l		0.085		0.164	0.027	0.004	0.002	0.002	0.091	0.002	<0.005
Cu^{2+}	mg/l		<0.005		<0.005	0.0013	0.0006	0.0004	0.0003	0.0008	0.0006	0.001
Ni^{2+}	mg/l		<0.05		<0.05	0.0048	0.0045	0.0039	0.0035	0.0046	0.0053	<0.001
Co^{2+}	mg/l		<0.01		<0.01	0.0013	0.0010	0.0009	0.0008	0.0013	0.0016	<0.0002
Pb^{2+}	mg/l		<0.05		<0.05	0.0015	0.0010	0.0027	0.0013	0.0011	0.0009	0.0029
Cr^{3+}	mg/l		<0.01		<0.01	0.0027	0.0050	0.0045	0.0042	0.0043	0.0029	<0.005
Mo^{6+}	mg/l		<0.20		<.20	0.0031	0.0043	0.0110	0.0050	0.0380	0.0028	<0.0003
Total cations	mg/l		1148.1		1192.4	761.5	700.7	486.6	465.8	664.8	716.6	581.2
Anions:												
Cl^-	mg/l	488.2	436.2	411.3	444.9	32.0	4.9	5.4	4.6	4.5	5.7	2.8
SO_4^{2-}	mg/l	1685.6	1666.0	1568.7	1833.0	1621.0	1621.0	1025.0	998.0	1485.0	1589.0	1437.0
HCO_3^{2-}	mg/l	839.4	725.8	711.9	616.2	172.0	143.0	139.0	141.0	138.0	116.0	<24.4
NO_3^-	mg/l		–		–	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	–
BO_3^{3-}	mg/l		26.33		27.90	0.94	0.65	0.73	0.54	0.58	0.33	<0.54
Total anions	mg/l		2829.6		2896.5	1826.5	1770.4	1170.9	1145.1	1629.0	1712.2	1464.4
Total analysis	mg/l		3977.8		4088.9	2588.0	2471,2	1657.5	1610.9	2293.9	2428.9	2045.6
Analytic. error	%		?		?	1.66	–0.69	2.24	1.17	0.20	0.89	–2.02
Chemical type		SO_4-Ca	SO_4-Cl-HCO_3-Ca	SO_4-Ca	SO_4-Cl-Ca	SO_4-Ca	SO_4-Ca	SO_4-Ca	SO_4-Ca	SO_4-Ca	SO_4-Ca	SO_4-Ca

[1] Experiment performed on November, 2021

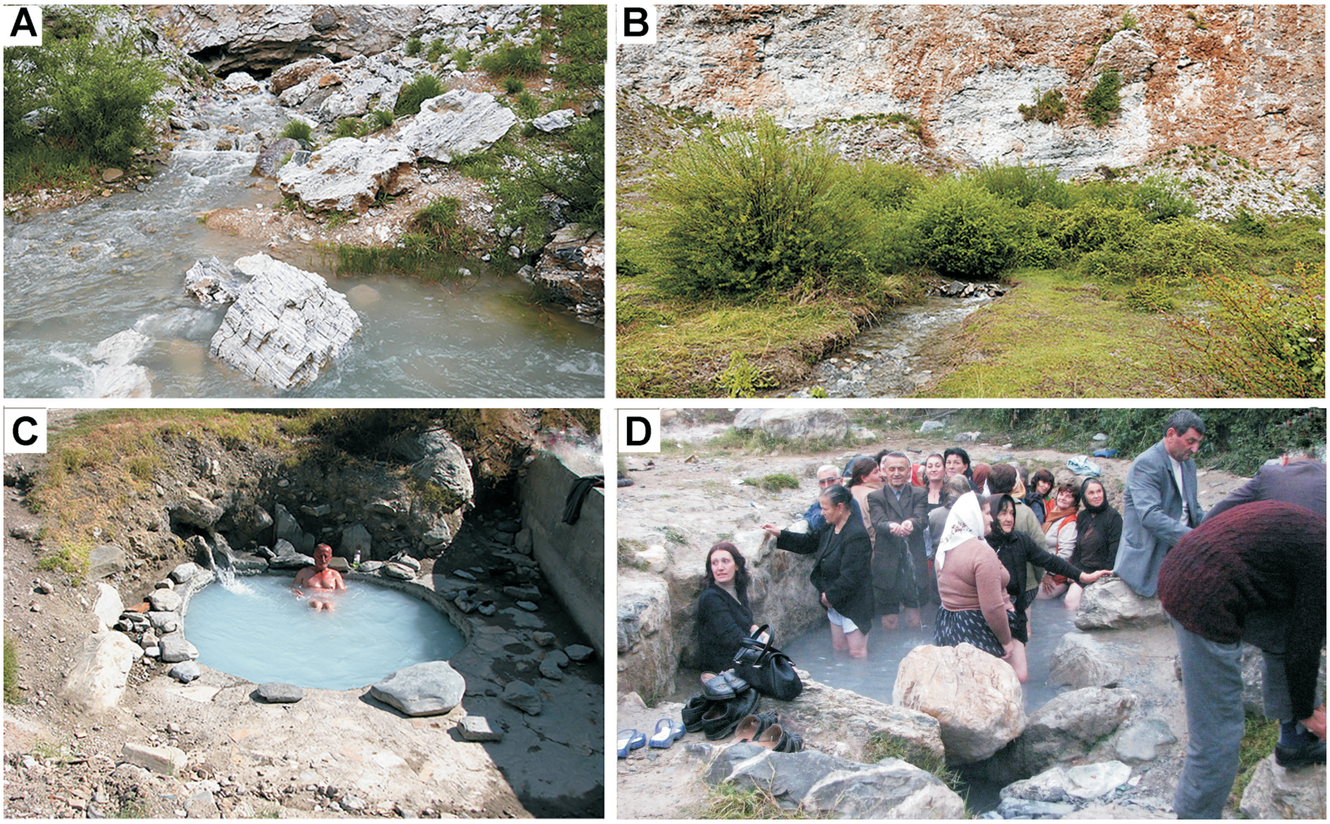

Fig. 7. Some important karst springs of the Peshkopi gypsum area

Cold brackish springs: **A** – Konri spring; **B** – gypsum temporary spring; **C** and **D** – thermal springs; some water escaping from the thermal spring intake structure is used by the local people for treatment in some improvised water pools (photos by V. Andreychouk – A and Band R. Eftimi – C and D)

The analyses are shown also in a Piper diagram (Fig. 8) showing the strong overlap of the two sets of chemical analyses, of 1957 and 2019.

COMPARISON OF HYDROCHEMICAL CHARACTERISTICS OF TWO GROUPS OF SPRINGS

Comparing the waters of the two groups of springs, cold brackish and thermal, one can clearly see differences between them in terms of pH, mineralisation (TDS), hardness and the content of major ions, that determine their hydrochemical type. The thermal waters are distinguished by a much higher content of individual components, primarily such as: Mg (89–95 compared to 6–37 mg/l), Na (254–267 compared to 1.13–5.25 mg/l), K (46–48 compared to 0.1–0.99 mg/l), Cl (436–445 compared to 4.5–5.7 mg/l), BO_3 (26–28 compared to 0.3–0.9 mg/l) (Fig. 9). The high content of Cl^+, Na^+ and other ions causes a change in the hydrochemical type of water from typically sulphate (SO_4-Ca) to types with a high chloride content (SO_4-Cl-HCO_3-Ca, SO_4-Cl-Ca). The concentration of barely soluble silica in the waters of the second group is clearly higher (55–58 compared to 3.9–9.5 mg/l).

Among minor components, differences lie in the significantly higher content of Li (0.958–1.021 compared to 0.003–0.093 mg/l), Sr (8.5–8.8 compared to 3.4–5.5 mg/l) and Mn (0.085–0.164 compared to 0.002–0.091 mg/l) in the water of the second group.

The water after experimental gypsum dissolution is poorly mineralised (TDS 2034 mg/l; EC 2240 µS/cm), very hard (TH 1433.5 mg$CaCO_3$/l), with a non-carbonate hardness of 28.67 mval/l, and weakly alkaline (pH 7.40). The redox potential corresponds to conditions ranging from oxidising to transitional, at the boundary between oxidising and reducing (Eh 179 mV). Among dissolved constituents in water, Ca (574 mg/l) and SO_4 (1437 mg/l) predominate, with Mg (0.62 mg/l) and Cl (2.8 mg/l) occurring in a very small amounts. Typical additional gypsum characteristics – Sr (6.57 mg/) and Ba (0.007 mg/l) – were found in the waters. According to Shchukariev's classification, they represent the SO_4-Ca type. The chemical composition of the experimentally obtained solution, the magnitudes and proportions of the components, are similar to the first group of studied waters (Table 1).

DISCUSSION

The similarity of the chemical composition of the waters of the first (cold springs) group to the artificially produced solution indicates the formation of the waters of this group in a shallow water circulation system. Such a system involves the infiltration of rainwater and surface water flowing from the higher parts of Mt. Korab into the gypsum and then the underground transport of water downward through channels in the gypsum and the drainage of water by springs flowing out at the foot of the massif

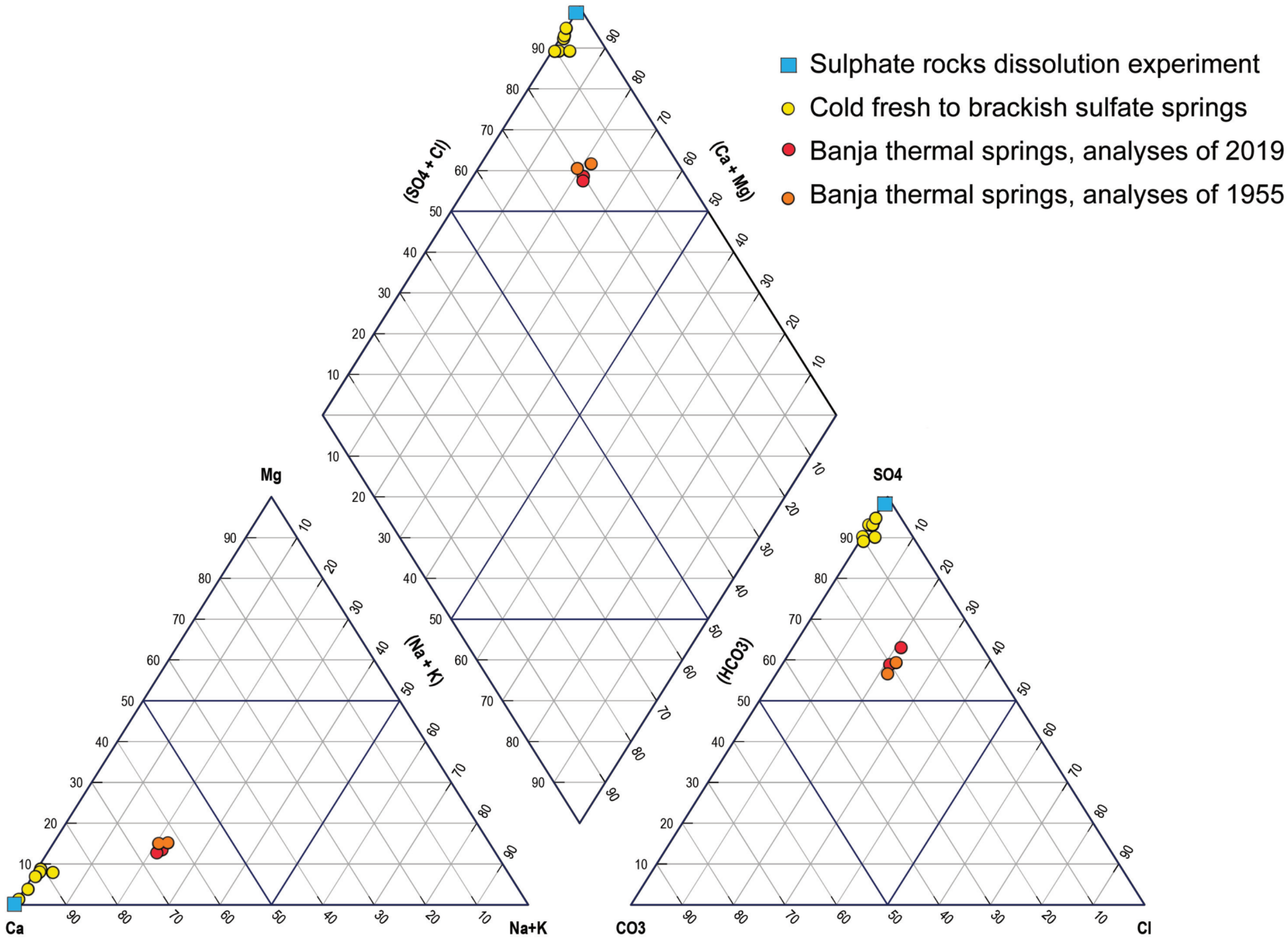

Fig. 8. Piper diagram of karst springs of the Peshkopi gypsum area

(Fig. 7). Such a circulation system predicts a simple pattern in the formation of the chemical composition of waters, because of the interaction of the waters with sulphate rocks.

The waters of the second (thermal springs) group represents the waters of the deeper circulation system. This is reflected by the temperature of the waters, exceeding 40°C, which classifies them as thermal waters. We also observe marked differences in chemical composition. The deeper-circulating waters are more strongly mineralised, with a lower pH, higher total and carbonate hardness and have near-reducing conditions. Significant differences are observed in the hydrochemical type of the waters. In general, the waters of the shallower circulation are of SO_4-Ca type and the waters of the second group are of SO_4-Cl-HCO_3-Ca and SO_4-Cl-Ca hydrochemical types. In addition, they are clearly enriched in SiO_2, Na, K, Mg and H_2S gas.

The presence of significant amounts of Na, Cl and BO_3 in them may indicate stagnant flow conditions. With depth and a slowdown in the rate of circulation, easily soluble salts begin to accumulate in the aquifers. Higher concentrations of dissolved silica may indicate dissolution at certain depths – with a higher temperature of the rock environment and a higher alkalinity of the solution (silica solubility increases with temperature and solution pH). The origin of the waters of this group from deeper aquifers is also indicated by the absence of nitrate contaminants.

In order to establish this thesis, a comparative statistical analysis of the chemical composition of the sampled waters and the experimental water sample was carried out. A greater similarity of the values of the individual components to the concentrations obtained in the experiment would increasingly indicate a shallow (near-surface) circulation of the waters and a shorter time for the formation of their chemical composition. Conversely, greater differences in the chemical composition of the waters indicate deeper and longer (in terms of time) circulation of water flowing from the given spring.

In order to compare the experimental results obtained with reference measurements, the measurements were first standardised by assuming the maximum result as 100%. Thus, values of variables between 0 and 1 were obtained, the results being differentiated. Such an approach ensures that each result has a significant influence on evaluation of conformity with the experimental results. The methodology is justified because samples were collected in the same way from each location, what makes this manner of standardisation appropriate. The errors related to sampling are the same on average and do not affect the conclusions. The depth of water circulation was neglected because the goal of the work was to compare the experimental results with all sources considered without their course being taken into consideration. The application of such methodology ensures that the condition of similarity of variance for all

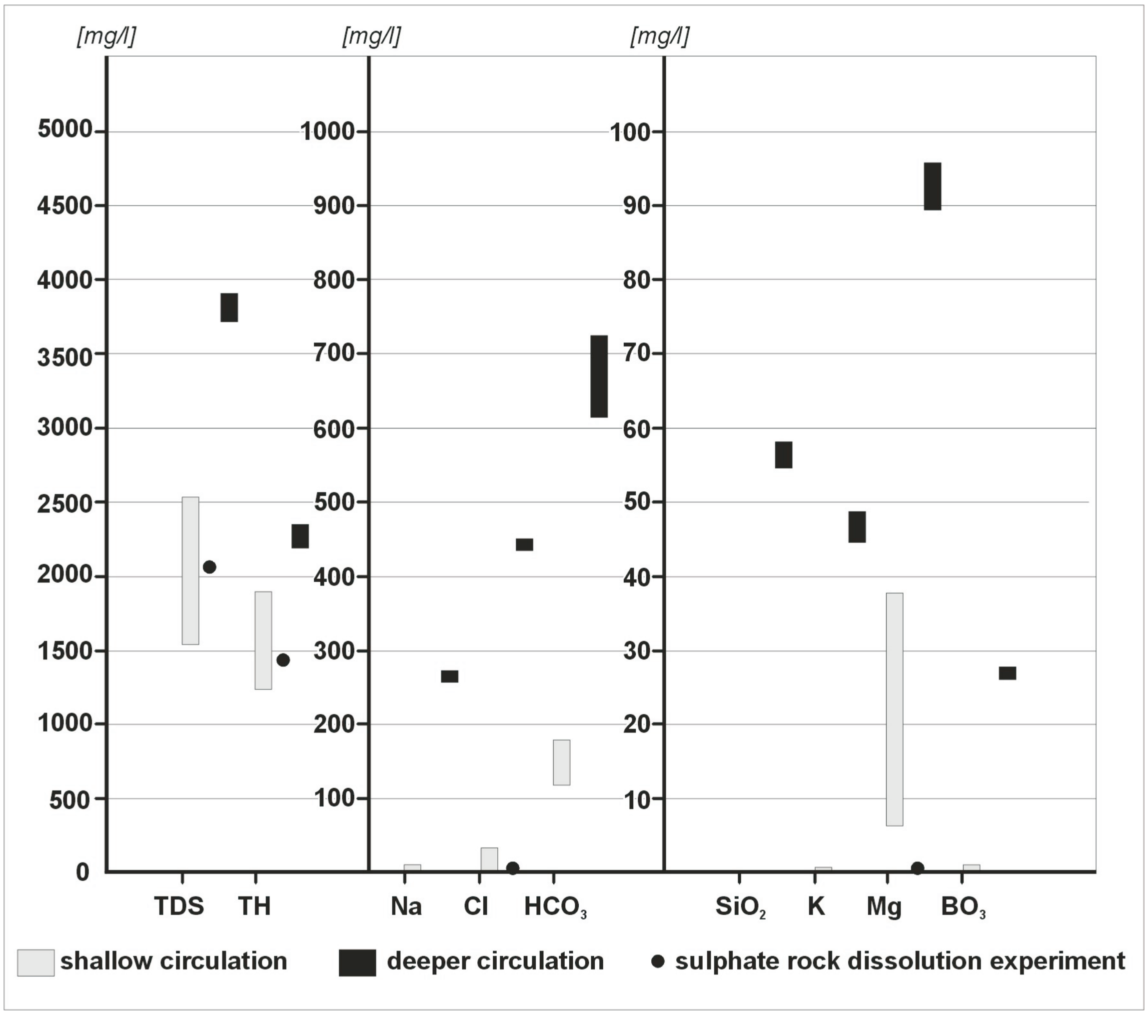

Fig. 9. Comparison of the chemistry of groundwater of shallow and deeper circulation in the anhydrite-gypsum rocks of the Peshkopi area

variables is met, which makes it possible to conduct a reliable correlation analysis. The results of each measurement after standardisation are shown in Table 2.

The highest results for individual parameters were found for both samples from Peshkopi. This means that their characteristics are significantly different from the others. To assess the similarity of the experimental results obtained, the mean square error (Chalton and Troskie, 2001; Castelazzo and Mitani, 2012) for each reference point was calculated according to the formula:

$$MSE_s = \sqrt{\frac{\sum_{i=1}^{31}\left(y_{emp} - y_{\exp}\right)^2}{n-2}};\ k = 1,...,8 \quad [1]$$

where: y_{emp} – empirical results; y_{exp} – experimental results; n – number of measurements; k – number of the variable (1 – Gipsi; 2 – Rabdisht; 3 – Belova; 4 – Konri; 5 – Brezdan; 6 – Vlesha; 7 – Banja 1; 8 – Banja 2).

Due to the incompleteness of the measurements, only those parameters that were measured for all nine samples (including the experimental one) were considered for comparison. The magnitude of analytical error was also not taken into account for the calculations. The results of the measurements are given in Table 3.

The standardised experimental results obtained deviate on average from the standardised measured results by ~12–14%. The smallest difference occurred for the Konri and Vlesha springs (12%), and the largest for both samples from the Banja springs (~76%). Samples from the Banja springs show completely different characteristics compared to the remaining samples. Most of the measured values from these springs gave the highest value compared to the other samples. In addition, a correlation analysis was conducted to test these observations. Table 4 lists the values of Pearson's linear correlation coefficients for each pair of variables.

The results obtained show that the linear correlation coefficient between the Konri measurements and the experimental results is the highest at ~95.3%. Significant values of the coefficient were also obtained for Vlesha (95%), Rabdisht i Gipsi (93%), Belova (91%) and Brezhdan (89.7%). For samples from Banja 1 and Banja 2, the correlation coefficients were statistically insignificant. For the Banja 2 sample, no correlation was found.

Table 2

Standardised measurement values for eight reference locations and for the experiment

Parameter	Units	1 Gipsi	2 Rabdisht	3 Belova	4 Konri	5 Brezdan	6 Vlesha	7 Banja 1	8 Banja 2	9 Experiment
pH		0.96282051	0.96666667	1	0.95512821	0.88333333	0.96410256	0.82051282	0.79487179	0.94871795
Eh	mV	0.71666667	0.65	0.67916667	0.74583333	0.84166667	0.72083333	0.1625	1	0.74583333
Total dissolved solids (TDS)	mg/l	0.41142636	0.39894248	0.57562548	0.62127934	0.64872324	0.61289657	0.95573897	1	0.52465824
Total hardness	$CaCO_3$ mg /l	0.53229582	0.51018727	0.71835443	0.76833709	0.81016993	0.77314895	0.96449627	1	0.62142362
Carbonate hardness	$CaCO_3$ mg/l	0.19146075	0.19431837	0.19011599	0.1970079	0.23701462	0.1598588	1	0.84905026	0
Non-carbonate hardness	mval/l	0.61837358	0.5892312	0.85706356	0.91867888	0.95920067	0.93727449	0.90480155	1	0.79572578
EC (25)	µS/cm	0.42065217	0.36847826	0.46956522	0.46086957	0.50217391	0.45869565	0.97826087	1	0.48695652
H_2SiO_3	mg/l	0.08617261	0.07755535	0.08444916	0.11374785	0.16372796	0.06721464	0.94007689	1	0.0034469
SiO_2	mg/l	0.08617718	0.07755946	0.08445364	0.11375388	0.16373664	0.0672182	0.94002068	1	0.00344709
Na^+	mg/l	0.01966292	0.01535581	0.01940075	0.01775281	0.0994382	0.00423221	0.95280899	1	0.00037453
K^+	mg/l	0.01981833	0.01300578	0.02043765	0.02002477	0.09186623	0.00206441	0.94549959	1	0.00412882
Li^+	mg/l	0.00783546	0.00685602	0.00685602	0.00685602	0.09108717	0.0029383	0.93829579	1	0.00489716
Ca^{2+}	mg/l	0.58856473	0.56746549	0.83328992	0.85907788	0.8958062	0.91716593	0.9688721	1	0.74693931
Mg^{2+}	mg/l	0.25676102	0.22971693	0.15552983	0.32400295	0.39092918	0.06776807	0.94317584	1	0.00652426
Ba^{2+}	mg/l	0.5	0.4	0.53333333	0.43333333	0.83333333	0.53333333	1	0.33333333	0.23333333
Sr^{2+}	mg/l	0.45147727	0.38772727	0.44238636	0.51761364	0.57875	0.53011364	0.96590909	1	0.74659091
Mn^{2+}	mg/l	0.01219512	0.01219512	0.55487805	0.02439024	0.16463415	0.01219512	0.51829268	1	0.0304878
Cu^{2+}	mg/l	0.08	0.06	0.16	0.12	0.26	0.12	1	1	0.2
Ni^{2+}	mg/l	0.078	0.07	0.092	0.09	0.096	0.106	1	1	0.02
Co^{2+}	mg/l	0.09	0.08	0.13	0.1	0.13	0.16	1	1	0.02
Pb^{2+}	mg/l	0.054	0.026	0.022	0.02	0.03	0.018	1	1	0.058
Cr^{3+}	mg/l	0.45	0.42	0.43	0.5	0.27	0.29	1	1	0.5
Mo^{6+}	mg/l	0.055	0.025	0.19	0.0215	0.0155	0.014	1	1	0.0015
Total cations	mg/l	0.40808454	0.39064072	0.55753103	0.58763838	0.63862798	0.60097283	0.96284804	1	0.48742033
Cl^-	mg/l	0.01213756	0.0103394	0.01011463	0.01101371	0.07192628	0.01281187	0.98044504	1	0.00629355
SO_4^{2-}	mg/l	0.55919258	0.54446263	0.8101473	0.88434261	0.88434261	0.86688489	0.90889253	1	0.78396072
HCO_3^{2-}	mg/l	0.19151281	0.9426839	0.19013502	0.19702397	0.23697988	0.15982364	1	0.84899421	0.03361808
BO_3^{3-}	mg/l	0.02616487	0.01935484	0.02078853	0.02329749	0.03369176	0.01182796	0.9437276	1	0.01935484
Total anions	mg/l	0.4042465	0.3953392	0.5624029	0.61122044	0.63058864	0.59112722	0.97690316	1	0.50557569
Total analysis	mg/l	0.40536575	0.39396904	0.56100663	0.60436792	0.63293306	0.59402284	0.97282888	1	0.50028125
Analytical error	%	1.34939759	0.70481928	0.12048193	-0.4156627	1	0.53614458	-0.8855422	-0.6807229	-1.2168675

Table 3

Values of mean square error for experimental results compared to individual reference variables

Springs	Gipsi	Rabdisht	Belova	Konri	Brezhdan	Vlesha	Banja 1	Banja 2
MSE	0.13	0.14	0.15	0.12	0.19	0.12	0.76	0.77

Table 4

Correlation matrix

Variable	The determined correlation coefficients are significant with $p < .05000$ N = 31									
	Mean	Stand dev	Gipsi	Rabdisht	Belova	Konri	Brezhdan	Vlesha	Banja 1	Banja 2	Experi-ment
Gipsi	0.289869	0.257577	1.000000	0.996235	0.910099	0.957719	0.928703	0.939854	–0.277543	–0.256852	0.929678
Rabdisht	0.269821	0.249284	0.996235	1.000000	0.915168	0.962522	0.920106	0.942288	–0.268673	–0.221061	0.930075
Belova	0.365368	0.306486	0.910099	0.915168	1.000000	0.935533	0.923265	0.941847	–0.322257	–0.164440	0.909795
Konri	0.362270	0.327892	0.957719	0.962522	0.935533	1.000000	0.959531	0.980616	–0.199063	–0.096725	0.952766
Brezdan	0.409539	0.325526	0.928703	0.920106	0.923265	0.959531	1.000000	0.968082	–0.239306	–0.268028	0.896781
Vlesha	0.345884	0.339624	0.939854	0.942288	0.941847	0.980616	0.968082	1.000000	–0.187802	–0.153383	0.949818
Banja 1	0.921497	0.169135	–0.277543	–0.268673	–0.322257	–0.199063	–0.239306	–0.187802	1.000000	–0.087114	–0.248407
Banja 2	0.960875	0.129480	–0.256852	–0.221061	–0.164440	–0.096725	–0.268028	–0.153383	–0.087114	1.000000	–0.001282
Experiment	0.301316	0.326364	0.929678	0.930075	0.909795	0.952766	0.896781	0.949818	–0.248407	–0.001282	1.000000

In summary, the analysis performed showed that the greatest convergence of experimental results with reference results was found for the Konri variable, and was slightly worse for other samples other than the Banja samples (1 and 2). For the latter, there was no convergence of results with the experimental samples. Similar observations can be made by analysing individual reference points and the relationships between them.

The hydrochemical testing conducted, together with the statistical analysis of the hydrochemical data, support the preliminary inferences of two systems of groundwater circulation in the anhydrite-gypsum succession in the Peshkopi region – shallow and deeper, which is reflected in the thermal properties and chemical composition of these waters. In the shallow circulation system, infiltration of rainwater and surface water flowing from the higher parts of the Deshat Korab Mountains into the gypsum occurs, followed by underground transport of water downwards to the drainage zone of the springs flowing at the foot of the massif.

In the deeper circulating system, water percolates deep into the anhydrite-gypsum succession and flows along the stratal dip up to the barrier in the form of the regional fault, which brings ascending water to the surface (see paragraph *Research area*). Geothermal waters, with a relatively high content of Na, K, Cl, BO_3 and dissolved SiO_2 thus migrate under pressure towards the surface. In the near-surface zone, they are cooled (to a temperature of ~40^0C) and diluted by the shallowly circulating cool sulphate waters of this zone. The general scheme of water circulation in the Peshkopi area is shown in Figure 7.

CONCLUSIONS

Geochemical and physicochemical studies, a sulphate rock dissolution experiment and statistical analysis of the hydrochemical data show the presence of two groundwater circulation systems in the anhydrite-gypsum deposits of the Peshkopi area: shallow and deeper.

The shallowly circulating waters are brackish, cool, and represent the hydrochemical type SO_4-Ca. The deeper circulating waters are more highly mineralized, with a lower pH, higher general and carbonate hardness; they represent reducing conditions, with SO_4-Cl-HCO_3-Ca and SO_4-Cl-Ca compositions. They are enriched in SiO_2, Na, K and Mg.

The water from the experimental dissolution of gypsum is poorly mineralized, very hard and weakly alkaline, representing the SO_4-Ca type. The redox potential corresponds to conditions ranging from oxidising to transitional. The chemical composition of the experimentally obtained solution, and the magnitudes and proportions of the components, are similar to the water of the shallow circulation system.

Comparison of the chemical composition of the waters analysed and the water sample from the experiment shows convergence of the experimental results with the reference results of most samples, except for the samples from representing thermal waters of Peshkopi area.

In the shallow circulation system, infiltration of rainwater and surface water flowing from the Korab Mountains into the gypsum occurs, followed by underground transport of water downwards to the drainage zone of the springs flowing at the foot of the massif. In the deeper circulation system, the water percolate deep into the anhydrite-gypsum deposits and flows along the slope of the rock layers up to the regional fault which brings ascending water to the surface. Geothermal waters migrate under pressure towards the surface, and in the near-surface zone they are cooled and diluted by the shallowly circulating sulphate waters of this zone.

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