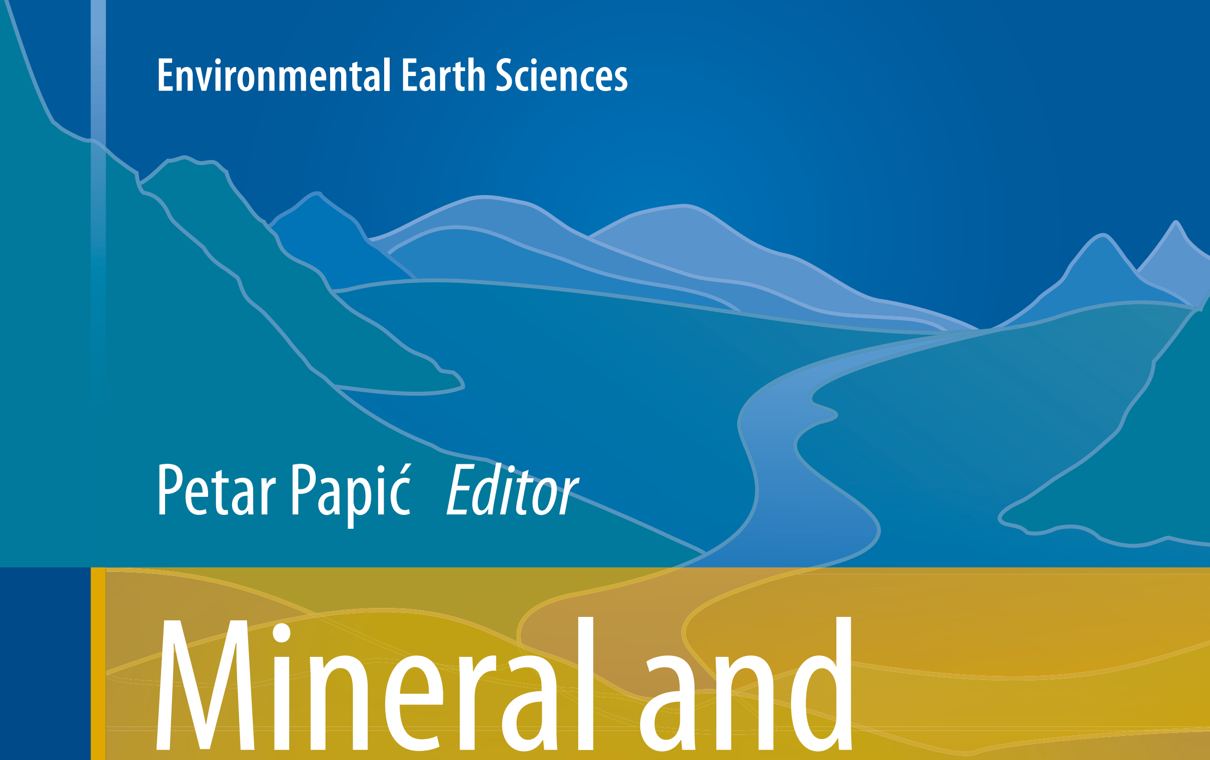

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Petar Papić *Editor*

Mineral and Thermal Waters of Southeastern Europe

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Petar Papić
Editor

Mineral and Thermal Waters of Southeastern Europe

Springer

Editor
Petar Papić
Department of Hydrogeology
Faculty of Mining and Geology
Belgrade
Serbia

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Preface

During the International Multidisciplinary Conference on Mineral Waters: Genesis, Exploitation, Protection, and Valorization, in Karlovy Vary from September 8–11, 2014, the Commission on Mineral and Thermal Waters (CMTW) held two meetings. Thanks to the chairman Dr. Jim LaMoreaux, the Commission accepted my offer to edit a book titled “Mineral and Thermal Waters of Southeastern Europe.” This book, published by Springer, is a part of the Environmental Earth Sciences Book Series.

The book is organized into nine chapters. It discusses the geology of SE Europe, mineral and thermal water potential, and physical and chemical properties, as well as the utilization of thermal and mineral waters in Albania, Bosnia and Herzegovina, Bulgaria, Croatia, Macedonia, Montenegro, Romania, and Serbia.

In my capacity as editor, I have included nearly 30 colleagues from eight neighboring countries, who are engaged in the fields of mineral water and geothermal energy. Some of them are young doctoral students who specialize in hydrogeology and hydrogeochemistry.

I am especially grateful to Dr. Jim LaMoreaux, for giving me the opportunity to be the editor, and to Dr. Annett Büttner, the publishing editor from Springer. I am indebted to all the authors who contributed to this book, including my doctoral students Ms. Maja Todorović and Ms. Marina Ćuk, who also helped with the layout and graphics and to Ms. Dubravka Miladinov for proofreading of the papers. My personal thanks go to Professor Dr. Miroslav M. Vrvić, from the Faculty of Chemistry, University of Belgrade, and to Mr. Petar Dopuđ from the mineral water bottling company “Dia Petra.”

I trust that the book will be useful not only to those who specialize in mineral waters, but also for other professionals as well.

Belgrade
September 2015

Petar Papić

Contents

Geology of South-Eastern Europe 1
Vladica Cvetkovic, Dejan Prelević and Stefan Schmid

Mineral and Thermal Waters in the Croatian Part of the Pannonian Basin 31
Staša Borović, Tamara Marković, Ozren Larva, Željka Brkić and Vinko Mraz

Thermal Waters in Bulgaria 47
Aleksey Benderev, Vladimir Hristov, Klara Bojadgieva and Boyka Mihailova

Mineral Waters of Montenegro 65
Mihailo Burić, Zoran Nikić and Petar Papić

Mineral and Thermal Waters of Serbia: Multivariate Statistical Approach to Hydrochemical Characterization 81
Maja Todorović, Jana Štrbački, Marina Ćuk, Jakov Andrijašević, Jovana Šišović and Petar Papić

Mineral and Thermal Waters of Romania 97
M. Rosca, C. Bendea and A.M. Vîjdea

Thermal Waters of Albania 115
Romeo Eftimi and Alfred Frashëri

Geothermal Potential of Macedonia and Its Utilization 131
S. Popovska-Vasilevska and S. Armenski

Mineral, Thermal and Thermomineral Waters of Bosnia and Herzegovina 147
Neven Miošić and Natalija Samardžić

Geology of South-Eastern Europe

Vladica Cvetkovic, Dejan Prelević and Stefan Schmid

Abstract The region of South-Eastern Europe (SEE) occupies an important segment of the Alpine–Himalayan collisional orogenic belt and consists of several Phanerozoic mobile belts. The SEE region inherits its geology from the evolution of the Vardar Tethys ocean, which existed in-between the Eurasian (Europe) and Gondwana (Africa) continental plates and which relicts presently occur along the Vardar–Tethyan mega-suture. This synthesis, therefore, consists of (1) pre-, (2) syn- and (3) post-Vardar–Tethyan geology of SEE. Pre-Vardar–Tethyan geology on the European side is reflected by geological units formed from Precambrian to Mesozoic times and include the Moesian platform, the Dacia mega-unit and the Rhodopes. On the Gondwana side, it is represented by the External Dinarides, the Dalmatian-Ionian Zone and Stable Adria (Apulia), all principally formed from Paleozoic to Mesozoic times. The Syn-Vardar–Tethyan units encompass the bulk of the geological framework of SEE. They are a physical record of the former existence of the Mesozoic oceanic lithosphere, being represented dominantly by ophiolites and trench/accretionary wedge (mélange) assemblages, which originated and were reworked during the life-span of the Vardar Tethys. The Post-Vardar–Tethyan geological evolution refers to the time period from the final closure of the Vardar Tethys until present. It comprises all rocks that stratigraphically overlie the Vardar–Tethyan mega-suture and seal the contacts between the mega-suture and the surrounding geological units. This is the time characterized by rapid extension coupled with exhumation of the lower crustal material, high heat flow, both intrusive and extrusive magmatism and considerable lithosphere thinning.

Keywords Geodynamics · Gondwana · Europe · Mesozoic · Tethys

V. Cvetkovic (✉) · D. Prelević
Faculty of Mining and Geology, University of Belgrade, Đušina 11,
11000 Belgrade, Serbia
e-mail: cvladica@rgf.bg.ac.rs

S. Schmid
Institut für Geophysik ETH, Zürich, Switzerland

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Introduction

The Synthesis' Approach

The current understanding of the geological evolution of South-Eastern Europe (SEE) is associated with still many open questions. This is due to either the lack of data or because the existing data are of variable quality in different regions. This volume is primarily designed to be of use for applied geologists, whose main interest is remote from geological and geodynamical details, in particular from interpretations that are surrounded by large controversy. In this context, the ultimate aim of this synthesis is to provide the hydrogeological and engineering geological community with a solid understanding about the present geological framework of SEE and about how it formed throughout the geological history, without addressing in detail still debated questions.

In general, the SEE region consists of several mobile belts that formed during the youngest geological history of the Eurasian continent when Alpine–Himalayan belt originated. There is a general consensus that this region evolved during Phanerozoic geodynamic events controlled by sea floor spreading, plate convergence and collision, which occurred between the Eurasian and African (Gondwana) continental plates (e.g. Blundell et al. 1992). This geodynamic regime—which is still active today in the southernmost part of the region, i.e. in the Hellenide trench—was particularly important during the last 200 m.y. It was directly associated with the opening and closure of a branch of the Mesozoic Tethys that separated the Eurasian continent and a promontory of Africa, referred to as Adria plate. We consider the evolution of this part of the Mesozoic Tethys, hereafter named the Vardar Tethys, a pivotal point for the explaining the geological history of the entire SEE region. This synthesis, therefore, consists of three major parts, in which (1) pre-, (2) syn- and (3) post-Vardar–Tethyan geology of SEE are explained. These parts refer to geological entities and rock masses that formed before this ocean opened, those that originated during its life-span and those formed after it had been closed, respectively.

In this geological presentation we compile the information from relevant geological and geotectonic syntheses of various parts of the SEE region. For the Dinarides-Albanides-Hellenides we mainly use the interpretations provided by Karamata (2006), Robertson and Shallo (2000), Schmid et al. (2008) and Robertson et al. (2009), for the Carpathians and the Balkanides we apply the views of Mahel (1973), Ivanov (1988), Săndulescu (1994), Kräutner and Krstić (2006) and Schmid et al. (2008), whereas for the Balkan orogen in Bulgaria and the Rhodopes we use the syntheses of Dinter and Royden (1993), Burchfiel et al. (2003), Burchfiel and Nakov (2015) and Burg (2011), among many others.

Definition of the Research Area

The boundaries of South-Eastern Europe may differ because of various geographic and political reasons. Here SEE comprises the area that generally coincides with the Balkan Peninsula (Fig. 1). The north-westernmost border of this area is located

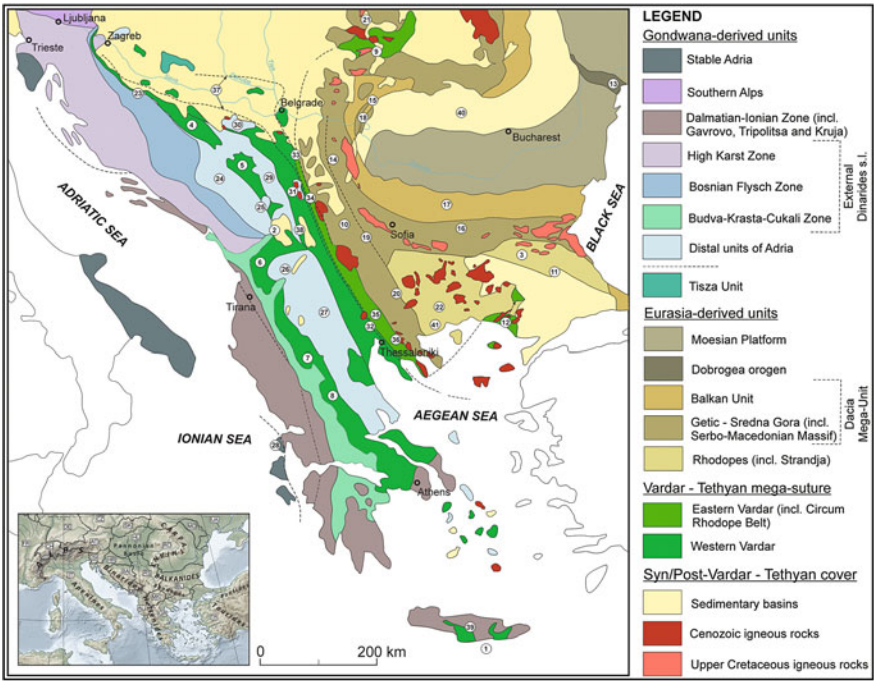

Fig. 1 A simplified geological sketch of South–Eastern Europe. The sketch is a modified compilation of the Geological Atlas of Serbia 1:2.000.000 (Dimitrijević 2002), the International Geological Map of Europe and Adjacent Areas (Ash et al. 2004), the Geological map of the Carpatho–Balkanides between Mehadia, Oraviţa, Niš and Sofia (Kräutner and Krstić 2006), and the Tectonic map of the Carpathian–Balkan mountain system and adjacent areas (Mahel 1973). Geotectonic and geological sketches of some parts of SEE by Schmid et al. (2008), Dimitrijević (1997), Karamata (2006), Robertson and Shallo (2000), and von Quadt et al. (2005) were also used. Explanations (by the order of appearance in the text): *1* Hellenic trench, *2* Metohija depression, *3* Maritsa valley, *4* Krivaja–Konjuh ultramafics, *5* Zlatibor ultramafics, *6* Mirdita ophiolitic massif, *7* Pindos ophiolitic massif, *8* Othrys ophiolitic massif, *9* Mureș valley (Transylvanian nappes), *10* Serbo–Macedonian Massif, *11* Strandja, *12* Circum–Rhodope belt, *13* North Dobrogea orogen, *14* Getic unit, *15* Danubian nappes, *16* Sredna Gora, *17* Balkan unit (Stara planina), *18* Ceahlău–Severin ophiolite belt, *19* Morava unit, *20* Vertiskos unit, *21* Biharia nappes, *22* Drama unit, *23* Sana–Una unit, *24* Central Bosnian Schist Mts. unit, *25* Lim Paleozoic unit, *26* Korabi unit, *27* Pelagonian unit, *28* Levkas island, *29* Jadar unit, *30* Drina–Ivanjica unit, *31* Kopaonik Mts. unit, *32* Paikon unit, *33* Kragujevac ophiolite complex, *34* Kuršumlija ophiolite complex, *35* Guevgelia–Demir Kapija ophiolite, *36* Eastern Hellenic ophiolites, *37* Sava Zone, *38* Kosovska Mitrovica Flysch, *39* Crete, *40* Dacic basin (Eastern Paratethys), *41* Mesta half– graben

south of Ljubljana and north of Istria, and its northern boundary is delineated by the Sava River, from Zagreb until its junction with the Danube, and further by the Danube River, all the way from Belgrade down to the Black Sea. The other borders of the SEE to the east, south and west are delineated by the coastal areas of the Black, Aegean, Ionian and Adriatic Seas, respectively. Politically, this region comprises the southern parts of Slovenia and Croatia, central and southern Serbia (including Kosovo), south-easternmost Romania (Dobrogea), the European part of Turkey, and the entire territories of Bosnia and Herzegovina, Montenegro, Albania and Greece.

In terms of present day geomorphology, the SEE region begins along the junction between the south-eastern Alps and the north-western Dinarides and encompasses the entire Dinaride–Albanide–Hellenide, Carpatho–Balkan and Rhodope mountain belts (see inset in Fig. 1). This rather complex orogenic realm contains a few smaller depressions, such as, for instance, the Metohija depression and the Maritza valley, whereas several lowlands occurring along the coastal areas are directly related to the above mentioned Seas. These recent depositional systems stay beyond the scope of this presentation.

Terminology

The specialists in applied geology usually face problems when acquiring a solid knowledge of the regional geological framework of a given area. This is so, because they are often bewildered by unnecessarily detailed geodynamic explanations or by too complicated and incomprehensible stratigraphic and lithological divisions. We think that a more simplified approach that follows a simple motto: ‘geology through geodynamics’, can be of use for those who may not be entirely familiar with recent developments in basic geo-disciplines. Therefore, we first briefly summarize essential theoretical aspects and explain the most important elements of the terminology used. This will surely strengthen the capability of future readers to follow our interpretations.

In a most simplistic way, the evolution of an orogen involves that two lithospheric plates, each having different stratigraphic and tectonic histories, approach each other and, finally, weld by collision (see Skinner et al. 2003). The process of ‘approaching’ occurs via subduction, by which usually oceanic areas in-between the converging continental plates often become totally consumed. After collision and welding the two once separated plates stick together, and this means that no intervening ocean exists anymore. What remains are relicts of the vanished ocean: different parts of the ocean’s bottom (mainly peridotites and basalts) and overlying sediments (cherts, various siliciclastic sediments, sometimes carbonates, etc.). Some of the originally intervening oceans do not disappear entirely via subduction but are obducted as huge ophiolitic sheets onto continental realms. Obduction means that the oceanic plate overrides the continent and during this process a mix of exotic rock masses that may represent any lithology derived from the margins of the colliding oceanic and continental plates is preserved. Such tectono-stratigraphically very complex mixed units underneath the obducted oceanic plates are referred to as ‘ophiolitic mélange’, whereas obducted peridotites are usually named ‘ophiolite’. An ophiolite basically represents a section of the Earth’s oceanic lithosphere that has been uplifted and exposed above sea level and often emplaced onto continental crust.

The above described orogen (i.e., a mountain belt) forming processes are commonly followed by post-orogenic phases, during which the earlier compression tectonics are replaced by strike-slip or purely extension regimes. This tectonic switch is mostly controlled by local changes in relative plate motions, and commonly evolves into gravitational (isostatic) instability and orogen collapse. The major driving force for the lithospheric extension is rapid advective thinning of the shortened thermal boundary conduction layer, which occurs beneath an orogen and causes a rapid uplift (Dewey 1988). In some places, the extension involves the formation of steeply dipping, crustal- to lithospheric-scale fractures, whereas in other places low-angle detachment faults substantially stretch the former orogen, exhuming deeper parts of the crust to the Earth’s surface. These exhumed parts are called ‘metamorphic core complexes’. These processes usually produce sedimentary basins and magmatism within transtensional/transpressional wrench corridors or within larger extensional areas.

In accordance to the explanations given above, the geology of SEE will be simply presented in terms of the formation of a complex mobile belt via disappearance of an earlier ocean. The term ‘orogen’ is used to delineate parts of this complex mobile belt, and always also has a geographical connotation (e.g. Dinaride orogen, Carpatho–Balkanide orogen, etc.). By the term ‘unit’ (or sometimes ‘mega-unit’) we delineate a geological entity formed during a similar time-span that has similar geotectonic and stratigraphic characteristics, but without implications whether that unit represents an earlier microcontinent or an erosion/tectonic window. In a similar way the terms: ‘mass’, ‘massif’, ‘block’, ‘belt’ or ‘zone’ are used. The notion ‘terrane’, however, is applied in the sense of Keppie and Dallmeyer (1990) and denotes a microplate that via subduction of a consuming oceanic was welded to (or docked to) another microplate or ‘terrane’. Note that the term ‘suture zone’—which normally represents a narrow belt located in-between two terranes, we here use in a wider sense, i.e. as ‘mega-suture’ for delineating the area that comprises all remnants of the Vardar Tethys. The main collision described below occurred between two large continental plates often also referred to as ‘Eurasia’ and ‘Gondwana’ (Fig. 1). The former is also named ‘European continent’, or simply ‘Europe’, whereas the parts of the latter present in SEE are referred to as Africa or its promontories, known as Adria or Apulia.

Geology of South-East Europe

Time-Space Framework of the Vardar Tethys Ocean

Geological development of the Vardar Tethys is still a matter of an ongoing debate (Karamata 2006; Robertson et al. 2009; Dilek and Furnes 2011). Therefore, we must first agree upon the most salient and widely accepted features of its evolution. For instance, there are conflicting opinions about how many oceans did exist in the SEE area. Some authors argue in favour of the existence of more than one ocean, suggesting that each left behind its own suture zone, whereas others believe that there was only one ocean and, consequently, only one suture. The latter consider many occurrences of ophiolites and ophiolitic mélanges as representing pieces of obducted oceanic lithosphere rather than suture zones. There are also disagreements with respect to the life-span of the ocean(s). Some authors suggest that the ocean (or more) opened in early- to mid-Triassic, others think that the Vardar Tethys' oceanic crust was present in SEE as early as in Paleozoic times. Most authors think that an oceanic realm of the Vardar Tethys was still open in the Late Cretaceous, whereas a minority still believes that the closure finished in Upper Jurassic/Early Cretaceous times. The above mentioned controversies are the subject of many papers (e.g.: Bernoulli and Laubscher 1972; Smith and Spray 1984; Săndulescu 1988; Robertson and Karamata 1994; Channell and Kozur 1997; Dimitrijević 2001; Golonka 2004; Haas and Pero 2004; Stampfli and Borel 2004; Bortolotti and Principi 2005; Schmid et al. 2008; Robertson et al. 2009, among many others). In these papers many different names appear for oceans and/or related ophiolites/ophiolite mélanges and suture zones, for instance: Neotethys (±Mesozoic Tethys), Vardar (±Axios), Dinaride (±Mirdita ±Pindos), Maliak-Meliata, Hallstadt, etc., and this adds to confusion and makes the comprehension of the already complex geology of this region even more difficult.

Although some of the above explained problematic issues will be addressed later (see section Syn-Vardar–Tethyan Geology of SEE), it is important to clearly state which scenario of the origin and evolution of the Vardar Tethys is adopted here. This starting point has important bearings to the entire division and organization of further geological presentation.

We base our simplified geological interpretation on a piece of information upon which most authors agree, namely on the view that there formerly existed *at least one ocean* in the region of present day SEE. It is generally referred to as Neotethys, and was distinguished from the Paleotethys whose remnants in Turkey and eastwards are uncontested by all authors. Furthermore, most authors agree that parts of the Neotethys Ocean remained *open during most of Mesozoic time*. Hence, our simple approach has similarities with the 'single ocean scenario', first proposed by Bernoulli and Laubscher (1972) and Baumgartner (1985), and recently refined and reformulated by Schmid et al. (2008). This scenario assumes that the (geographically) multiple belt of ophiolites and ophiolitic mélanges—stretching all the way from north-western Dinarides to Southern Greece (and further to Turkey and Iran), encompasses remnants of a single ancient oceanic realm—Neotethys, hereafter named Vardar Tethys. In this sense, this entire ophiolite-bearing complex orogenic belt can be considered a single very wide Vardar–Tethyan mega-suture. The western margin of this mega-suture is marked by the westernmost occurrences of the Jurassic ophiolites and ophiolitic mélanges in Bosnia (Krivaja–Konjuh), west Serbia (Zlatibor), east Albania (Mirdita) and central Greece (Pindos and Othris). The western margin terminates in the north-west at around Zagreb, whereas the eastern margin is buried beneath the thick cover of Pannonian sediments and reappears in the Mures valley, as part of the Transylvanian nappes (Balintoni 1994). This entire and very wide mega-suture zone crosses the Aegean Sea and outcrops again in Asia Minor of Turkey.

Summarizing, the geological division which follows invokes that: (1) all Mesozoic geological units located within the Vardar–Tethyan mega-suture are rock masses that formed during the life-span of this Mesozoic ocean, (2) all pre-Mesozoic geological entities that primarily occurred on both sides of the ocean record parts of the Pre-Vardar–Tethyan geological history, and (3) all geological units that seal the contacts of the mega-suture and its shoulders are results of post-Vardar–Tethyan geology. In the presentation that follows these three time periods are ordered chronologically.

Pre-Vardar–Tethyan Geology of SEE

Pre-Vardar–Tethyan geological record is predominantly found in the areas west and east from the main mega-suture. These two broad continental margins underwent different geological evolutions during Paleozoic and pre-Paleozoic times. In the division below, the pre-Mesozoic geological entities located eastward from the mega-suture represent relicts of the southern margin of the ancient European continent (Eurasia), whereas the units outcropping on the western/south–western side of the mega-suture are parts of the northern margin of Gondwana or its promontories (Adria or Apulia). In addition, several pre- to early Mesozoic geological units presently outcrop within the mega-suture itself. Some authors (see Robertson et al. 2009 and references therein) interpret these units as terranes—i.e. as microcontinents, which once separated different oceanic realms. As already mentioned above, we here adopt a scenario in which these basement units are considered distal parts of the Gondwana margin, i.e. distal parts of Adria (see section Pre-Vardar–Tethyan geology of the Gondwana continent and Fig. 1).

It needs to be stressed that the pre-Vardar–Tethyan geological history of both sides of the major mega-suture is difficult to discern, because the geological records are only fragmentarily exposed and because they were later subject to different periods of tectonic and sedimentary reworking. This is especially valid for the Gondwana margin, because during the syn- and post-Vardar–Tethyan time, this area underwent deposition of platform carbonates and locally siliciclastic sediments. Although also partly obscured, the pre-Vardar–Tethyan geological record on the European side is better exposed and it provides evidence that this area evolved through geodynamic processes similar to those related to the SEE geological evolution, characterized by the disappearance of oceanic realms and collisional accretion of continental units to the European mainland.

Pre-Vardar–Tethyan Geology of the European Continent

Pre-Vardar–Tethyan geology on the European side is reflected by geological units formed from Precambrian to Mesozoic times. These complex units occur within three mega tectonic continental blocks: the Moesian platform, the Dacia mega-unit (including the Serbo–Macedonian Massif) and the Rhodopes (including Strandja). These individual units represent huge and more or less complex nappe piles, which differ in their age and geological evolution and whose remnants discontinuously appear below a Mesozoic and younger cover. Note, however, that the Circum–Rhodope Belt (Kauffmann et al. 1976), which fringes part of the Serbo-Macedonian Massif and the Rhodopes in northern Greece, is not considered here as part of the European margin but as an element of the main mega-suture (see further below).

The Moesian Platform in SEE comprises the regions of northern Bulgaria and South Dobrogea in Romania. It is now largely covered by younger sediments and its basement is reconstructed on the basis of scarce exposures as well as by boreholes and seismic data. Moesia is the only tectonic unit of the present SEE, which was part of the European continent during significant portion of Paleozoic and Mesozoic times (Seghedi 2001). It has acted as the margin of stable Europe since Jurassic Cimmerian orogeny that only marginally affected it and whose remnants presently occur in north Dobrogea. With respect to Vardar–Tethyan geology, the Moesian Platform can be regarded as ‘undeformed foreland’ (Schmid et al. 2008). It is composed of Neoproterozoic (‘Panafrican’) metamorphic rocks that only locally record a Variscan overprint (Seghedi et al. 2005; Oczlon et al. 2007). Most of the deformation of the South Carpathians and the Balkanides has occurred along the boundaries of the stable Moesian platform (Fügenschuh and Schmid 2005).

In contrast to predominantly covered Moesia, the metamorphic basement of the Dacia mega-unit outcrops in many places. In Serbia, this unit corresponds to the area between the eastern border of the mega-suture (i.e. Eastern Vardar) and the Moesian Platform, which integrates two systems of nappes: the Serbo-Macedonian Massif and the East Serbian Carpatho–Balkanides. Towards the south they form two branches: one goes directly southwards, as the continuation of the Serbo–Macedonian Massif in the Former Yugoslav Republic (FYR) of Macedonia and Greece, and the other continues south-eastwards, and merges with the composite Balkan unit in Bulgaria (Burchfiel and Nakov 2015). Across the Danube, the Dacia mega-unit continues to the north–east into the South Carpathians of Romania, whereas in the north it is bordered by another European mega-unit named Tiszia (e.g. Csontos and Vörös 2004). The Tiszia unit is outside of the SEE region and will not be addressed in this study.

The internal part of Dacia consists of the East Serbian Carpatho–Balkanides—often referred to as the Getic unit and the Danubian nappes, according to Romanian nomenclature, and by their lateral counterparts in Bulgaria—the Sredna Gora unit and the Balkan unit (or Stara Planina). More eastern analogues of these units can be found in the Pontides of NW Anatolia. These individual geological entities are, in fact, poorly exposed collages of Paleozoic units and/or terranes that have a Gondwana affinity. The units often have local names, for instance: Median Dacides—Danubian (Vrška Čuka–Miroč)—central/pre-Balkan or Infrabucovinian—Getic (Kučaj)—Kraishte–Sredna Gora units, etc. The contacts between them are obscured by later compressive tectonics and by deposition of a younger Mesozoic and Cenozoic sedimentary cover. The largest preserved suture-like belt is the one composed of Iuti–Donji Milanovac–Deli Jovan–Zaglavak–Černi Vrah gabbro-diabase (±peridotite) complexes. The Deli Jovan complex is dated to Early Devonian (Zakariadze et al. 2012), which suggests that these so-called "Danubian Ophiolites" represent relicts of an Ediacarian-Early Cambrian ocean and magmatic complex (Kounov et al. 2012). Where exposed, the Dacia-derived basement is represented by medium- to high-grade Neoproterozoic ('Panafrican') to Early Paleozoic gneiss and Paleozoic greenschist to sub-greenschist metabasic rocks. The basement is unconformably overlain by Late Carboniferous to Permian fluvial sediments (Iancu et al. 2005), with detrital material derived from the European continent. The basement is also intruded by Variscan plutons that crop out at many places in Serbia (e.g. Neresnica, Gornjani, Ziman, etc.; Šarić et al. 2014) and Bulgaria (e.g. Vezhen, Hisara, Smilovene, etc.; Carrigan et al. 2005). Large parts of the Dacia mega-unit were separated from the European continent along the Ceahlau-Severin oceanic rift which extends from Ukraine into north-westernmost Bulgaria. The closure of this basin in the Lower Cretaceous was followed by later phases of emplacement of these nappe systems from the Late Cretaceous to Miocene times (Săndulescu 1984; Kräutner and Krstić 2006; Burchfiel and Nakov 2015).

The Serbo–Macedonian Massif represents the structurally uppermost part of Dacia and a more internal unit with respect to the above described Carpatho–Balkanides and is comparable to the Supragetic nappe of Romania (Schmid et al. 2008). It is a crystalline belt of Paleozoic-age high to medium grade metamorphic rocks that are generally distinguished into the Lower and the Upper Complex (Dimitrijević 1957, 1997). The Lower complex is composed of gneiss, micaschists and subordinate amphibolites, quartzites, marbles and migmatites. They occur as relicts of a Late Neoproterozoic-earliest Cambrian high- to medium-grade metamorphic belt that formed during the Cadomian orogeny and which underwent overprints in Variscan and Alpine times (Balogh et al. 1994). The rocks of the Upper Complex represent a Cadomian volcano-sedimentary sequence, which was only metamorphosed under greenschist facies conditions. They are intruded by Cadomian igneous rocks and are covered by post-Cambrian sedimentary series (Kräutner and Krstić 2002). According to most authors the Bulgarian part of the Serbo–Macedonian Massif in Bulgaria is also known as the Morava unit (Kounov et al. 2004), whereas in Greece this same massif is referred to as Vertiskos Unit (i.e. Kockel et al. 1971, although some authors interpret Vertiskos as being part of the

Rhodopes (Burg 2011). The northern continuation of the Serbo–Macedonian Massif is documented in the drill-cores in the Pannonian basin (e.g. Kemenci and Čanović 1997) and its northern counterparts outcrop again as part of the Biharia nappes of the Apuseni Mountains (sensu Schmid et al. 2008).

The most internal Europe-derived geological units in the south-east are the very complex tectonic units of the Rhodopes and overlying Strandja. In the east, large parts of the Rhodopes are covered by Cenozoic basin sequences. However, due to post-thickening extension of the Rhodopes starting in the Eocene, various originally deep-seated high- to medium-grade metamorphic rocks became exhumed and are now exposed in the mountains of southern Bulgaria and northern Greece (Burg 2011). According to many authors the Rhodope massif comprises a south- to southwestward facing nappe stack. However, north-facing tectonic transport has also been documented in the Rhodopes, particularly in the Eastern Rhodopes (Bonev et al. 2015). There is also an ongoing debate about the origin of thin ophiolitic bodies found within the Rhodopes. According to some (e.g. Froitzheim et al. 2014), these have their origin in the "Vardar Ocean", i.e. in our Vardar–Tethyan mega-suture. Classically, they were attributed to a former Mesozoic Ocean located between the main part of the European continent and a more southerly located continental block named Drama block, which is still of European affinity and is located north of the Vardar–Tethyan mega-suture (e.g. Turpaud and Reischmann 2010).

The Rhodope massif underwent high- to ultra-high pressure metamorphism (Liati and Seidel 1996; Mposkos and Kostopoulos 2001; Kostopoulos et al. 2003), supposedly at various times starting in the Jurassic, and was subsequently overprinted by granulite and amphibolite facies (Liati and Seidel 1996; Carrigan et al. 2002; Liati et al. 2002). Similarly to the Carpatho-Balkanides, the Rhodope massif is also pierced by Variscan intrusives (e.g. Arda and Startsevo; Cherneva and Gheorgieva 2005). This suggests that Variscan late- or post-collision granitoid magmatism is a common feature for the European part of the pre-Tethyan basement, as was found in other parts of the Alpine orogen (e.g. Finger et al. 1997). The Rhodopes are separated from the overlying Strandja unit by Jurassic thrusts and often by younger Cenozoic faults (Kilias et al. 1999; Georgiev et al. 2001; Okay et al. 2001; Brun and Sokoutis 2007; Bonev et al. 2015). Strandja is part of the north-verging Cimmerian orogen. This basement-cover unit is formed by northward-verging nappes in Late Jurassic to Early Cretaceous time. From this time onwards, the Strandja belongs to the Balkan part of the complex Alpine–Himalayan mobile belt.

Pre-Vardar–Tethyan Geology of the Gondwana Continent

Pre-Mesozoic outcrops presently occurring westwards from the main mega-suture represent remnants of the northern margin of the ancient Gondwana continent. In this synthesis we distinguish three major tectonic entities, namely: the External Dinarides sensu *lato*, the Dalmatian-Ionian Zone and Stable Adria (Apulia).

The External Dinarides *s.l.* are composed of a system of westward-vergent Mesozoic and younger nappes. Their Paleozoic basement is scarcely exposed, predominantly in form of tectonic or erosion windows. This basement records only weak metamorphism in Variscan times, with again a weak metamorphic overprint in Cretaceous and Cenozoic times (Pamić et al. 2004; Hrvatović and Pamić 2005). It comprises separate Paleozoic units, such as Sana-Una, Central Bosnian Schist Mts. and Lim Paleozoic, which occur from Croatia, through Bosnia and Herzegovina, Montenegro to SW Serbia. The hemipelagic Pindos Zone stretches from Greece to Montenegro, but disappears NW-wards south of Dubrovnik. The more external hemipelagic Ionian Zone, crossing the Adriatic Sea SE-wards from Italy into Albania is only exposed in Albania and Greece. Its pre-Mesozoic basement, however, is completely covered by Mesozoic carbonate platform sediments (Robertson and Shallo 2000). In front of the Ionian Zone one enters the Apulian carbonate platform exposed on Ionian islands (e.g. Levkas). This platform sequence is part of the Adria/Apulia plate, which acted as the main indenter along which the External Dinarides and more internal units, as well as the Alps were deformed (Schmid and Kissling 2000). In this context, the immediate basement of the Ionian zone, which possesses the structurally lowermost position, is represented by Pre-Apulia and Apulia and can be correlated by non-deformed parts of Istria (Stable Adria in Fig. 1).

As noted earlier, several continental blocks are located within the mega-suture itself and they are considered as distal parts of the ancient Gondwana margin. These basement units include (from NNW to SSE): Jadar, Drina-Ivanjica, and Kopaonik Mts. (including the Studenica slice) in Serbia, Korabi in Albania, and Pelagonia in the FYR of Macedonia and Greece. All these units are predominantly composed of non- to low-grade metamorphic Paleozoic clastic sediments overlain by Permian/Triassic carbonates that are often transformed into marbles and intercalated with rift-related igneous rocks (Zelić et al. 2005; Sudar and Kovács 2006; Schefer et al. 2010). The south-eastern counterparts of these units are the Korabi and Pelagonian zones that mostly occur in Eastern Albania and Greece. Both the Korabi and Pelagonian zones record a more pronounced Variscan metamorphic and magmatic overprint and show transitions from an arc to a passive margin setting (Clift and Robertson 1990; Robertson and Shallo 2000). The Pelagonian zone is intruded by Variscan granitoids (Mountrakis 1984), similar outcrops are not present in situ in the Korabi zone. However, granitoids of a similar age are found as allochthonous blocks within the ophiolite mélange sequences in west Serbia or as pebbles in the sequence overlying mélange (e.g. Neubauer et al. 2003). All the above mentioned Paleozoic/earliest Mesozoic basement units were originally overlain by westward obducted ophiolites, but they acquired their present structural setting by later out-of-sequence thrusting, mostly during the Latest Cretaceous to Early Cenozoic.

Syn-Vardar–Tethyan Geology of SEE

This geological evolution is characterized by the formation of ophiolitic rock masses during the opening of the Vardar Tethys in mid-Triassic time until its final closure in the late Mesozoic. These ocean-derived rocks presently occur within the mega-suture either as parts of mostly allochthonous sequences, reworked during collision and afterwards, or as predominantly autochthonous series that overlie the pre-Mesozoic basements of the Gondwana and European margins. We begin with the mega-suture itself, because this is the area which hosts all the remnants of the Mesozoic Vardar Tethys.

Syn-Vardar–Tethyan Geology of the Mega-Suture

The Vardar–Tethyan mega-suture consists of lithologies that physically record the former existence of Mesozoic oceanic lithosphere. In general, they are represented by ophiolites and trench/accretionary wedge (mélange) assemblages. Although it is a highly heterogeneous rock association, all its lithological members have in common that they either originated or were reworked/displaced during the life-span of the Vardar Tethys, including its closure via subduction, obduction and collision processes.

In terms of geographic distribution, at least three subparallel ophiolite belts are distinguished, each spatially associated with their mélanges. The easternmost ophiolitic sub-belt is known as Eastern Vardar (also called Main Vardar by some authors, see Dimitrijević 1997). In Serbia and FYR of Macedonia it occurs as a narrow and N-S elongated ophiolite belt and it widens from the Belgrade area north–eastwards into Romania. In the east, it is in direct contact with the Serbo–Macedonian Massif, and in the west it is often delineated by overlying Senonian flysch sediments, as well as by the contact with the above described parts of the distal Adria (e.g. Kopaonik Mts. and Paikon unit). The Eastern Vardar comprises small occurrences near Kragujevac and Kuršumlija in Serbia and larger masses near Demir Kapija and Guevgelia in FYR of Macedonia and those of the easternmost Hellenic ophiolites in the Thessaloniki area. The northern continuation of this zone is covered by the Pannonian sediments (Čanović and Kemenci 1999), but the belt crops out again as part of Transylvanian nappes in the Apuseni Mts. (Săndulescu 1984; Balintoni 1994). Further to the south, this unit grades into the so-called Circum–Rhodope Belt (Kockel et al. 1971; Michard et al. 1994; Meinhold and Kostopoulos 2013)—a belt that consists of a mixture of ophiolitic rocks and rocks of the European continental margin. This belt is called Circum–Rhodope because it surrounds the Rhodopes in the west (Thessaloniki area), south (NE Greece) and in the east (easternmost Bulgaria), where it links with the Strandja orogen. Structurally, Strandja overlies the Rhodope unit. The Eastern Vardar consists of igneous ophiolite members, mainly basalt, diabase and gabbro, whereas peridotites are remarkably rare. The rocks possess the strongest supra-subduction zone (SSZ) affinity of all the ophiolites from this region (Brown and Robertson 2004; Šarić et al. 2009; Božović et al. 2013), indicating that large parts of them formed in the upper plate of an intra-oceanic subduction zone. The age of formation of the ophiolites is mid-Jurassic and their final emplacement age is constrained as uppermost Jurassic by both stratigraphic (Bortolotti et al. 2002; Săsăran 2006; Kukoč et al. 2015) and radiometric evidence (Anders et al. 2005; Božović et al. 2013). Although, some authors (e.g. Schmid et al. 2008) argue that the Eastern Vardar ophiolites are the structurally highest tectonic entity within the Dacia mega-unit and that they were probably obducted onto the European Margin, its original emplacement is still a matter of debate (Petrović et al. in press).

Going westward, the next ophiolite belt encountered is the Western Vardar ophiolite belt and even further west one finds the Dinaride-Mirdita-Pindos ophiolite belt (e.g. Jones and Robertson 1991; Lugović et al. 1991; Beccaluva et al. 1994; Shallo 1995; Bazylev et al. 2009). These two belts occupy gradually more external positions with respect to the main axis of the Balkan Peninsula and are geographically separated by the outcrops of Drina–Ivanjica–Korab–Pelagonia Paleozoic basement of distal Adria, and its Mesozoic cover. The Western Vardar ophiolites comprise large predominantly ultramafic massifs in Serbia (Maljen, Stolovi, Kopaonik Mts., etc.) and smaller masses in FYR of Macedonia and Greece (e.g. Almopya). The most prominent peridotites massifs of the Dinaride–Mirdita–Pindos ophiolite belt are the Krivaja–Konjuh massif of Bosnia and Herzegovina, the Mirdita–Tropoja, Kukes, Bulquiza massifs of Albania and the Pindos and Vourinos massifs of Greece. As already mentioned, these two ophiolite belts are best regarded as parts of the same piece of the Vardar Tethys oceanic lithosphere, which was more or less uniformly obducted towards the west, i.e. onto the passive margin of the Gondwana continent. Hence, we agree with the view of Schmid et al. (2008) that these ophiolites should be collectively named Western Vardar to distinguish them from the Eastern Vardar ophiolites. The view of a single Western Vardar ophiolite belt is supported by the following observations: (a) these ophiolites are predominantly represented by large ultramafic bodies, whereas pillow basalts, diabases and gabbros are subordinate, (b) the ultramafic slices were emplaced as hot plates that produced so-called 'metamorphic sole assemblages' at their base, some of them displaying classical inverted P-T gradients (e.g. Brezovica; Karamata 1968), (c) the metamorphic sole rocks exhibit similar age ranges (Lanphere et al. 1975; Okrusch et al. 1978; Spray et al. 1984; Dimo-Lahitte et al. 2001; Bazylev et al. 2009), and (d) the ophiolites show a continuous change in composition, going from west to east, from a mid-ocean-ridge- (MOR) to a supra-subduction zone (SSZ) geotectonic affinity (Maksimović and Majer 1981; Bortolotti et al. 2002). Some of the westernmost ophiolite occurrences, such as parts of the Krivaja-Konjuh massif in Bosnia and Herzegovina and Ozren in SW Serbia exhibit an extremely fertile geochemical signature typical of subcontinental lithospheric mantle (Bazylev et al. 2009; Faul et al. 2014). Thus, when also including the Eastern Vardar into consideration, it is clear that all SEE ophiolites show a general compositional shift from west to east: from the least-depleted subcontinental mantle-like peridotites, through typical MORB ophiolites and transitional MORB–SSZ ones up to those that exhibit a pronounced SSZ affinity.

Besides the above described remnants of the bottom of the Vardar Tethys, represented by pieces of lithospheric mantle (ultramafics) and overlying oceanic crust (gabbro-diabase-basalt), the syn-Vardar–Tethyan geology is recorded by rocks of subduction trench and accretionary wedge assemblages. In the Serbian literature, this series is commonly named Diabase–Hornstein-, Diabase–Chert or Diabase–Radiolarite Formation (Kossmat 1924; Ćirić and Karamata 1960) and we here refer to it as ophiolitic mélange. The main substrate of the mélange is represented by Upper Jurassic terrigenous sediments deposited in a tectonically active subduction trench. They consist of a non-metamorphosed to slightly metamorphosed silty material mostly derived from volcanic rocks and basalts, which encloses up to several meters long lenses or boudin-like blocks of sandstones (±conglomerates). This terrigenous matrix hosts blocks (olistoliths) with sizes varying from several meters up to a few tens of meters, which show variable lithologies, such as pillow-, massive- and hyaloclastic basalt and radiolarite (both Triassic and Jurassic), gabbro-diabase, serpentinite, and rare granitoids. At some places, this heterogeneous association also comprises several tens of km long masses of Triassic limestone. These are either products of gravitational gliding into the trench in which case are named olistoplaques (Dimitrijević and Dimitrijević 1973) or, alternatively, they were tectonically sliced off the Gondwana margin during obduction (Schmid et al. 2008). At a late stage during obduction the trench sediments and ophiolitic mélanges were obducted by the large and still hot ultramafic bodies of the Western Vardar oceanic lithosphere and this produced the already mentioned contact-metamorphic rocks known as metamorphic soles.

Syn-Vardar–Tethyan Geology of the European Side

During most of the Mesozoic the European continental margin predominantly acted as the eastern passive margin of the Vardar Tethys. In the Early Triassic continental red beds were deposited over the basement of the Dacia mega-unit. In Middle to Late Triassic, this sedimentation gradually evolved into the deposition of shallow marine limestones, and deposition of terrestrial sandstones continued throughout the Early Jurassic (‘Gresten facies’). Later on, the basin suddenly deepened, giving way to Middle Jurassic deposition of radiolarite and Late Jurassic/Early Cretaceous deposition of pelagic sediments. The main phase of east-directed (in present-day coordinates and in Eastern Serbia) nappe stacking formed during the mid-Cretaceous (so-called “Austrian” phase). This is evident from the age of a post-tectonic cover composed of Albian to Cenomanian Molasse-type deposits that are widespread in the Romanian Carpathians. Locally, however, this part of the European continent was also affected by Late Cretaceous deformation (“Laramian” phase), as pointed out by Săndulescu (1984). Due to late uplifts of the more distal (more frontal) parts of the European margin, such sedimentary record is rare in the Serbo–Macedonian Massif and in the Rhodopes.

The record of active subduction processes along the western margin of the European continent is found in the Eastern Vardar Zone. It was related to the formation of the Paikon arc (Brown and Robertson 2004) in the mid-Jurassic. This arc is considered to be a short-lived feature, because soon after its formation, it was influenced by slab rollback and spreading behind the arc. This led to the formation of the oceanic crust preserved in the Demir Kapija and Guevgelia ophiolites in FYR of Macedonia (Božović et al. 2013).

Syn-Vardar–Tethyan Geology of the Gondwana Side

The rock record of the Permian to Triassic intracontinental rifting phase, by which the Vardar Tethys formed, is abundant on the Gondwana side of the mega-suture. In addition to many places in the mega-suture itself, from NW Bosnia and Herzegovina to Greece, these rocks crop out throughout the External Dinarides *s.l.* in Croatia, Bosnia and Herzegovina and Montenegro. These are mostly autochthonous rock sequences that consist of shallow-water marine/lagoonal limestones, often with gypsum layers, and continental siliciclastic sediments. They are associated with predominantly mid-Triassic volcanic and volcaniclastic rocks that range widely in composition from tholeiitic to calc-alkaline and from basalt to rhyolite (Pamić 1984). The Triassic of the proximal parts of the Gondwana margin was characterized by deposition of thick shallow-water carbonate sediments (Rampnoux 1970), whereas at more distal places continental slope facies or even basinal facies deposited, for instance Ladinian/Carnian siliceous limestones (Dimitrijević and Dimitrijević 1991; Schefer et al. 2010). This deposition continued into the Jurassic and produced thick radiolarite sequences in Bosnia and SW Serbia (Rampnoux 1970; Pamić 2000; Vishnevskaya and Đerić 2005).

In the Late Jurassic, huge masses of ophiolites were obducted to the west and covered large parts of the eastern distal margins of the Gondwana continent. By later out-of-sequence trusting these obducted ophiolites were deformed and at places also dismembered and these tectonic and subsequent erosion processes left parts of the underlying basement exposed. This post-obduction thrusting also affected narrow deep-water intervening basins. One such basin is, for instance, the Budva Zone in Montenegro, Krasta–Cukali Zone in Albania and the Pindos–Olonos Zone in Greece (Robertson and Shallo 2000; Schmid et al. 2008). Some of these basins, such as the “Flysch Bosniaque” (Aubouin et al. 1970) continue to be active from the latest Jurassic into the Cenozoic, although varying both along and across strike with respect to paleotectonic conditions and source areas (see explanations in Schmid et al. 2008).

Post-Vardar–Tethyan Geology of South-East Europe

The post-Vardar–Tethyan geological evolution refers to the time period from the final closure of the Vardar Tethys until present. It comprises all rocks that stratigraphically overlie the mega-suture and seal the contacts between the suture and the surrounding geological units. The oldest unconformable cover of the mega-suture is represented by Tithonian reef limestones and Lower Cretaceous flysch-like clastic sediments. From this, one could theoretically infer that all geological formations that are younger than the Lower Cretaceous would naturally belong to the post-Vardar–Tethyan geology. However, this is not so simple because not all the elements of the mega-suture closed in Late Jurassic to Early Cretaceous. Therefore, we must face a still open question, namely: did the entire Vardar Tethys close by uppermost Jurassic/lowermost Cretaceous times or, alternatively, did some of its realms floored by oceanic crust remain still open throughout the Late Cretaceous or even later? In other words, at what time does the post-Vardar–Tethyan geology really start?

The Late Cretaceous, Its Magmatism and the Problem of the Sava Zone

Late Cretaceous time was a period of formation of widespread flysch sediments, whose remnants are mostly preserved in the Serbian and Macedonian part of the Balkan Peninsula. They were deposited within deep and elongated troughs that post-date obduction. Some of these flysch sediments are only slightly deformed, others are strongly deformed and they all passively overlie the ophiolites, ophiolitic mélange and basement rocks of the Adria distal margin, as already noticed by Kossmat (1924). One narrow belt called Sava– or Sava–Vardar zone (Pamić 2002) begins south of Zagreb and stretches WNW-ESE towards Belgrade, and then apparently inflects and continues as a very narrow strip further southward to FYR of Macedonia (Fig. 1). Its continuation can be further traced in the Izmir area of Western Turkey (Bornova flysch of Izmir Ankara suture Zone; Okay et al. 2012). The southward narrowing and almost disappearance of the Sava zone may have resulted from substantial compression and uplift of the southern parts of the Balkan Peninsula in latest Cretaceous to Paleocene times. The Sava zone is younger and locally more metamorphosed than other Cretaceous flysch belts overlying the Jurassic mélanges, particularly in Northern Bosnia where upper greenschist to lower amphibolite facies metamorphism of late Cretaceous age was reached (Ustaszewski et al. 2010). Because it contains blocks of Late Cretaceous ophiolite-like basalt–diabase(±gabbro) complexes (Karamata et al. 2005; Ustaszewski et al. 2009; Cvetković et al. 2014), some authors believe that the Sava zone is the last suture that records the former presence of a Tethyan oceanic realm throughout Late Cretaceous times (Karamata 2006; Schmid et al. 2008; Robertson et al. 2009).

The geotectonic significance of the Sava zone is crucial for elucidating the entire post-Vardar–Tethyan geological history. Many authors (see Gallhofer et al. 2015) invoke that Late Cretaceous subduction of Sava zone oceanic lithosphere was responsible for the formation of well-known Late Cretaceous Banatite–Timok–Srednjegorje magmatic and metallogenetic belt (Berza et al. 1998; von Quadt et al. 2005). This is a presently curved but originally straight (Fügenschuh and Schmid 2005) belt that developed within the Dacia-derived basement of the European margin. It is part of a global subduction belt along the Eurasian active margin, which can be further traced to the Pontide magmatic arc in Anatolia, and the Somkheto–Karabakh arc in Lesser Caucasus (e.g. Ciobanu et al. 2002; Georgiev et al. 2009; Mederer et al. 2013, and references therein). It consists of volcano-sedimentary complexes formed during Turonian to Campanian times within elongated rift-like basins (Kräutner and Krstić 2006). The predominant rocks are andesite to basaltic/andesite volcanics and volcaniclastics associated to rare plutonic counterparts. This magmatism produced some of the largest porphyry copper systems in Europe, such as Bor, Majdanpek and Veliki Krivelj in Serbia and Assarel, Chelopech and Elatsite in Bulgaria, and some of them are related to significant epithermal gold deposits (e.g. Neubauer and Heinrich 2003). The magmatism shows a strong subduction geochemical affinity and that is explained by an eastward subduction under the European continent (Kolb et al. 2013; Gallhofer et al. 2015). This view is supported by the well-established across-arc age pattern that shows a gradual trenchward younging, in present-day coordinates westward in East Serbia and southward in Bulgaria (von Quadt et al. 2005; Kolb et al. 2013). In this context, if the Sava zone indeed hosts remnants of a wide Late Cretaceous oceanic bottom, then it is a suitable candidate for subduction and formation of the above mentioned magmatic and metallogenetic belt.

Cenozoic: Period of an Unstable Orogen, Widespread Magmatism and Formation of Extensional, Sedimentary Basins

The last chapter of the geological history of SEE involves the final consumption of Tethyan oceanic remnants and the still ongoing shaping of the global Alpine–Himalayan orogenic belt. The large amount of information ensures that the youngest geology is well-known, but this does not necessarily mean that the Cenozoic geological interpretation is simple. On the contrary, there are many controversies about this geological era as well, and, in keeping with our general approach, we will base our interpretation only on the issues upon which most authors agree.

Geotectonic Regime in the Cenozoic

During the Cenozoic, the just consolidated Dinaride–Albanide–Hellenide–Carpathian–Balkan section of the Alpine–Himalayan orogenic belt underwent remarkable tectonic reworking. The tectonics was controlled by various factors, ranging from global and regional to purely local in character. The essential tectonic control is the ongoing N- to NW-directed movement of the Adria microplate as an

African promontory. This is the major factor of compressive forces in the region, which led to substantial shortening in the coastal areas of Montenegro, Albania and Greece. However, since the beginning of the Cenozoic, this general compression has been associated by numerous regional-scale plate reorganizations and changes in local tectonic conditions. This made possible that a region undergoing a constant northward push from the south was able to evolve into local strike-slip or even purely extensional tectonic regimes, for instance in the Pannonian basin and the Aegean. These extensional episodes also involved differential rotations of some tectonic blocks along stable indenters and this primarily shaped the present day configuration of the SEE orogenic system. As the consequence of the opening of the Pannonian basin, the orogen split into two branches west and northwest of Belgrade—the Dinarides and the Carpathians including the Apuseni Mountains. Parts of the orogenic system exhibit remarkable curvatures due to oroclinal bending around Moesia and Adria as stable indenters, in the east and west, respectively (e.g. Fügenschuh and Schmid 2005). The (micro)plate re-organizations were also responsible for establishing regional to local geotectonic regimes, which ranged from pure compression to transpression in some regions, and transtension to pure extension in others.

The above mentioned controlling factors and resulting regional to local tectonic regimes were of supreme importance for the SEE Cenozoic geological evolution. In the area west of the Vardar–Tethyan mega-suture and along the Adriatic and south-Aegean coasts (e.g. Crete) the post-Vardar–Tethyan evolution was dominated by constant crustal shortening and westward and southward out-of sequence thrusting (see also above). This thrusting was associated with the formation of flexural foreland basins that likely existed from Middle/Late Eocene to Quaternary (Tari 2002; Merlini et al. 2002). This is corroborated by the evidence of compression tectonics in the SE continuation in Albania and in the Adriatic Sea (Carminati et al. 2004; Picha 2002). On the other hand, along the Vardar–Tethyan mega-suture and eastwards from it different tectonomagmatic conditions prevailed. They gave rise to widespread magmatism and formation of continental depositional systems. In the following text we illuminate only these two latter aspects of the SEE geology.

Cenozoic Sedimentary Basins

The formation of the Cenozoic sedimentary basins in SEE was primarily related to transtension and extension-related deformations that occurred from the Paleogene onwards. This was generally associated to a constant westward to southward retreat of E-, NE- to N-dipping subduction fronts, either as true oceanic plate subductions (subduction *s.s.*) or as deep underthrustings of thinned continental lithosphere (subduction *s.l.*). In response to this retreat, the respective suprasubduction/backarc areas underwent gravitational collapse and local spreading of previously thickened continental crust segments. In spite of this generally uniform tectonic framework, these extensional or extension-like pulses developed diachronously in different SEE regions, and these variations were controlled by the nature of the retreating subduction (oceanic vs continental lithosphere) and by local crustal anisotropy of the pre-Cenozoic basement. In this context, we distinguish the Cenozoic Dacic basin, and North and Southern Balkan Extensional Sectors (Rögl 1999; Burchfiel et al. 2003, 2008).

The Cenozoic Dacic basin is the western part of what is generally known as Eastern Paratethys (Rögl 1999). It was a wide sedimentary area, which was left behind from the much larger Vardar Tethys and since the Oligocene it acted as an isolated basin floored by continental crust. Most parts of the Eastern Paratethys occur outside of the northern boundary of SEE as defined in this article, and it will not be further addressed.

The Balkan Extensional Sector also created the Metohija depression and going north, encompasses much of the territories of Bosnia and Herzegovina and Serbia. It formed during the phase of opening of intramontane basins in the Dinarides, within a NNW-SSE wrench corridor associated to steeply dipping normal faults (Marović et al. 1999). The main tectonic cause for this event was a dual one: (1) the westward, and in Greece southward, retreat of the subduction front, associated to underthrusting of thinned continental crustal slices in the External Dinarides and Hellenides, which gave rise to gravitational subsidence in the overlying plate, and (2) retreat of the European slab underneath the Carpathians and opening the Pannonian basin. The same tectonic conditions were responsible for more or less contemporaneous magmatism (discussed below). The Northern Balkan Extensional Sector that underwent a strong tectono-sedimentary and magmatic overprint by the influence of the Pannonian extension led to exhumation processes and the formation of metamorphic core complexes along low-angle normal faults (Marović et al. 2007; Schefer et al. 2010; Matenco and Radivojević 2012).

The Southern Balkan Extensional Sector comprises Albania, FYR of Macedonia and the south–western parts of Bulgaria and north-western Greece. Post-orogenic sedimentary basins in this sector began to form in the late Eocene, when numerous NW-striking lacustrine basins formed. They were associated to extensional half-graben structures that originated in the eastern part in the FYR of Macedonia. Roughly simultaneously, similar basins formed in Bulgaria along NW-striking and W-dipping detachments, such as, for instance the large Mesta half-graben (Burchfiel et al. 2003; Kounov et al. 2004). This extensional phase produced several kilometers thick piles of Priabonian (Late Eocene) to Oligocene clastic and volcaniclastic deposits. Evidence of earlier extensions further east in the eastern Rhodopes is not entirely certain (Dimov et al. 2000). The second period started in Middle Miocene, after a short-lived compression event when the earlier sedimentary strata deformed by west-vergent structures (Dumurdzanov et al. 2005; Nakov et al. 2001), and also partly uplifted and eroded. Further to the west the Middle Miocene sedimentary phase produced heterogeneous types of basins, with the predominance of N-W-trending grabens. From the Late Miocene to the present day, in eastern FYR of Macedonia and adjacent Bulgaria E-W stretching normal faults and half-graben structures originated.

Cenozoic Magmatism

The immense subduction system of Eurasian continental active margin (e.g. Richards et al. 2012) entered its waning stage by the end of the Cretaceous. In the Upper Cretaceous occurred slab retreat and arc migration to the south and this, first changed fore-arc areas into arc regions (Kolb et al. 2013; Gallhofer et al. 2015; Gülmez et al. 2015) and then the entire arc system terminated by collision. During Cenozoic times this process continued to be the major mechanism of accommodating most of the shortening of an accretionary wedge of stacked nappes. These nappes represent the crustal portions decoupled from the underthrusting oceanic or continental lithospheric slab (Faccenna et al. 2003; Ricou et al. 1998; Schmid and Kissling 2000). The rolling-back of this slab, sometimes combined with its break-off and/or tear, produced rapid extension coupled with exhumation of the lower crustal material and high heat flow, which, in several areas ultimately gave rise to intrusive and extrusive magmatism (Bird 1979).

This magmatism is derived from both the mantle and the crust, and the rocks produced are geochemically extremely heterogeneous. In general, there is a roughly expressed age shift towards the west and south in Serbia and Bulgaria and Greece (and further in Western Anatolia), respectively. However, this shift is at many places obliterated because of magmatic events that were apparently controlled by regional- to local tectonic pulses. Additionally, there are substantial differences between this part of the Alpine–Himalayan orogenic magmatism and the classical active-margin or island-arc plate-tectonic models. It is so because in the former case the lithospheric slab(s) involved in subduction and roll-back processes was comprised of lithospheric mantle usually accompanied by lower crustal material generated by decoupling from the rest of the overlying crustal segments. Such subducting “lithospheric slab” is not simply a “wet oceanic lithosphere” that dehydrates and releases water necessary for melting of the overlying subarc asthenospheric mantle wedge. By contrast, in case of a delaminated slab melting is triggered when the asthenospheric mantle directly invades into the subcontinental lithosphere previously enriched in hydrous minerals or even into lower continental crust. Such complex geodynamic settings provided conditions for activation of different mantle and crustal sources and generation of wide spectra of mafic and intermediate to acid post-collisional magmas in the SEE region.

The above tectonomagmatic conditions resulted in formation of a large and diffuse zone of Eocene to Oligocene, subordinately Oligocene-Miocene igneous rocks. It stretches from the Periadriatic Province of the Alps up to the easternmost parts of the Macedonian–Rhodope–North Aegean Belt (Marchev et al. 2013). The belt continues further to East in the Thrace and Pontides volcanism in Turkey, and has its continuation in northwest Anatolia. The rocks are compositionally very heterogeneous, but there is apparent predominance of granitoid intrusives and associated acid to intermediate volcanic rocks.

The granitoid plutons were emplaced at mid-crustal levels, and have been exhumed by extension tectonics. They mostly occur along the Serbo–Macedonian Massif and the Circum–Rhodope Belt (e.g. Kopaonik Mts., Surdulica, Sithonia, Ouranopolis, Ierissos, etc.), within the Rhodope unit (e.g. Vrondou, Pirin, etc.) and smaller masses in the Kraishte and Sredna Gora tectonic units. They are dominantly I-type metaluminous, calc-alkaline to high-K calc-alkaline granites, granodiorites and tonalities, locally adakitic in character. Minor S-type intrusions, mostly Miocene in age, are found in Cyclades and Serbia. The origin of the I-type granitoids involves mixing (±fractional crystallization) between a mafic magma, derived by melting of a subduction-enriched depleted lithospheric mantle, and voluminous crustal felsic magma generated by melting of lower- to mid-crustal amphibolites (Perugini et al. 2003; Christofides et al. 2007, and references therein). The transition from non-adakitic to adakitic compositions is explained by amphibole fractionation of primary mantle-derived melts (Marchev et al. 2013). The origin of S-type magmas is modelled by melting of variable mid-to shallow crustal sources (Altherr and Siebel 2002; Cvetković et al. 2007).

It is widely accepted that the high-heat flow and melting associated to the formation of the Eocene-Miocene I-type intrusives did not result solely from thermal relaxation after tectonic thickening. By contrast, the melting of deep to middle crustal sources was most likely triggered by advective heating from mantle-derived melts. This means that mantle melting processes were essential for the petrogenesis of the origin of the I-type post-collisional granitoids, either by direct producing parental magmas, or by providing an advective heat source for melting of overlying continental crust (e.g. Pe–Piper and Piper 2002). There is a line of evidence for the presence of roughly contemporaneous mafic magmas in most post-collisional granitoid complexes in the SEE region, with omnipresence of mafic enclaves varying in composition from diorite to lamprophyre (Knežević–Đorđević et al. 1994; Prelević et al. 2004).

From the Oligocene to recent times occurred widespread volcanism in the SEE region. This volcanism was associated to the formation of numerous volcanic landforms, including stratovolcanoes, collapsing calderas, lava flows and various volcaniclastic facies and subvolcanic intrusions. The volcanoes occur within the same NW-SE directed belt as do the above described intrusives and host some very large volcanic areas in Serbia (e.g. Rudnik, Kopaonik, Lece, etc.), FYR of Macedonia (Kratovo–Zletovo) and Bulgaria (e.g. Zvezdel, Madzharovo, etc.). Although there is a general southward (westward) younging, there is no simple age-geochemical pattern among volcanic rocks. However, the ignimbrite flare-up is characteristic for the inception of extensional tectonic processes, which occurred in the late Oligocene-early Miocene. This was followed by the formation of a variety of subalkaline, potassic to ultrapotassic magmas, which indicates a progressive dehydration of the subcontinental lithospheric mantle. The youngest magmas were less voluminous, silica-undersaturated and sodic-alkaline in composition, suggesting a transition from lithosphere to asthenosphere melting in the orogenic environment. Generally, the volcanism shows orogenic geochemical features, characterized mostly by (high-K) calk-alkaline acid/intermediate volcanic rocks that are found intimately associated, in space and time with shoshonitic and ultrapotassic rocks.

One important consequence of the general geodynamic processes that triggered widespread volcanism within SEE may be an overall thinning of the lithosphere. As already mentioned above, during the interaction between the asthenosphere and lithosphere driven by rolling back of the delaminating lithosphere, previously metasomatized lithospheric domains hosting geochemically enriched material (with or without lower crustal segments) will be molten and removed due to the heat from the upwelling asthenosphere. In other words, we may expect thinning of considerable part of the lithospheric mantle, as being proposed for Western Anatolia (e.g. Kind et al. 2015) and the Pannonian basin (Horváth 1993; Falus et al. 2008), which resulted in increased heat flow. Available data for the thickness of the modern lithosphere in the central part of the SE Europe (Serbia, FYROM) based on the crustal temperature distribution, implies an approximate lithospheric thickness to be largest under the External Dinarides, where it is up to 260 km, whereas the large-extent thinning has been proposed for the Pannonian Basin and the Serbian–Macedonian Massif, with only 40–50 km (Milivojević 1993).

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Mineral and Thermal Waters in the Croatian Part of the Pannonian Basin

Staša Borović, Tamara Marković, Ozren Larva, Željka Brkić and Vinko Mraz

Abstract Favourable geothermal properties which are characteristic of the major part of the Pannonian Basin System also extend into its south-western margin where Croatia is situated. Owing to a thin lithosphere, the geothermal heat flow is high, which enables groundwater to heat up. Some of the natural geothermal springs have a millennial tradition in different modes of utilization. The mode of utilization varies according to the temperatures, e.g. waters of lowest temperatures (17–20 °C) are used for fish farming, while waters of the highest temperatures (68–98 °C) are utilized for space heating and hot water preparation. In total, thermal waters in Croatia are utilized in the following ten activities: recreation, balneotherapy, water heating, space heating, greenhouse heating, fish farming and directly as sanitary water, public water supply and bottled table and mineral water. According to the major ionic composition, waters belong to the NaCaMg–HCO_3SO_4, CaMgNa–HCO_3SO_4, CaMgNa–HCO_3, CaMg–HCO_3, NaCa–HCO_3 or Na–Cl-type. Despite significant potential confirmed through multiple professional and scientific studies, the utilization of both thermal and mineral waters remains at low levels and traditional applications.

Keywords Mineral waters · Thermal waters · Geothermal properties · Hydrogeochemical properties · Utilization · Pannonian basin · Croatia

Introduction

The existence of thermal water springs in Croatia can be traced via the incidence of toponyms *toplica/e*, meaning hot water spring/s, and *topličica*, meaning warm water spring (diminutive refers to lower water temperature). Some of the localities have been utilized even in prehistoric time (Šimunić 2008). Before the Roman Empire, a

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S. Borović · T. Marković (✉) · O. Larva · Ž. Brkić · V. Mraz
Croatian Geological Survey, Milana Sachsa 2, 10000 Zagreb, Croatia
e-mail: tmarkovic@hgi-cgs.hr

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number of Illyrian tribes populated areas of present day Croatia. One of the tribes occupied specifically the north-western part, with 25 natural warm and hot springs. They became known as *Iassi* all around ancient Europe (Schejbal 2003). Their name derives from the Greek root –ias/–iatria, meaning cure, because they were medicine–men using hot water healing powers. The same root is present today in the form iatros—physician (e.g. paediatrician). This fact shows that even before the arrival of the Romans, thermal springs had a specific place in the cultural landscape of the area. During the Roman Empire they were curative destinations, especially *Aquae Iassae* (Varaždinske toplice), *Aquae Balissae* (Daruvarske toplice), *Aquae Vivae* (Krapinske toplice), *Aquae Vitae* (unknown location) and *Ad fines* (Topusko), with many archaeological remains standing to this day. Mineral springs can also be recognized through toponyms. Highly mineralized cold springs are deemed Slatina (literally salty spring) and Kiselica (sour spring), referring to high dissolved CO_2 gas. They have been utilized for drinking and bottling for centuries as well.

Since thermal and mineral waters have been utilized during a vast time period in the present-day Croatian territory, it is clear that researchers were devoted to their exploration. The oldest chemical analyses date back to the last decades of the 18th century (Crantz 1777). In that period, mostly chemists and medical doctors were showing interest in the subject due to applications in balneology. Comprehensive geological research started at the end of the 19th century (Pilar 1884; Koch 1889; Voyt 1890), but reached its peak during the 1970s oil crisis. At that time the Federative Republic of Croatia (then a part of Yugoslavia) established a fund dedicated specifically to the exploration of thermal and mineral water. Major research results were summarized in a monograph "Geothermal and mineral waters of the Republic of Croatia" (Šimunić 2008), to avoid unnecessary repetition of work, since it provides a broad overview of the existing bibliography. The possibilities of geothermal energy utilization were analysed in the Geoen-Programme of geothermal energy utilization (EIHP 1998), as well as in a number of professional and scientific publications mentioned later in the text.

The aim of this paper is to give an overview of the occurrences of thermal and mineral waters in the Pannonian part of Croatia, their characteristics, utilization, sustainability issues and predictions of future development.

Geological Settings

Croatia is situated at the junction of major European regions: Alps, Dinarides and the Pannonian Basin System (PBS) (Fig. 1a). It is divided distinctively into two parts: the Pannonian part in the north–east and the Dinaridic part in the south–west (Fig. 1b). The north-eastern part of Croatia represents the south-western margin of the Pannonian Basin System (PBS), and the majority of Croatia's geothermal potential is concentrated there. It is characterized by high average geothermal gradient (49 °C/km) and surface heat flow (76 mW/m^2) (EIHP 1998). Conversely,

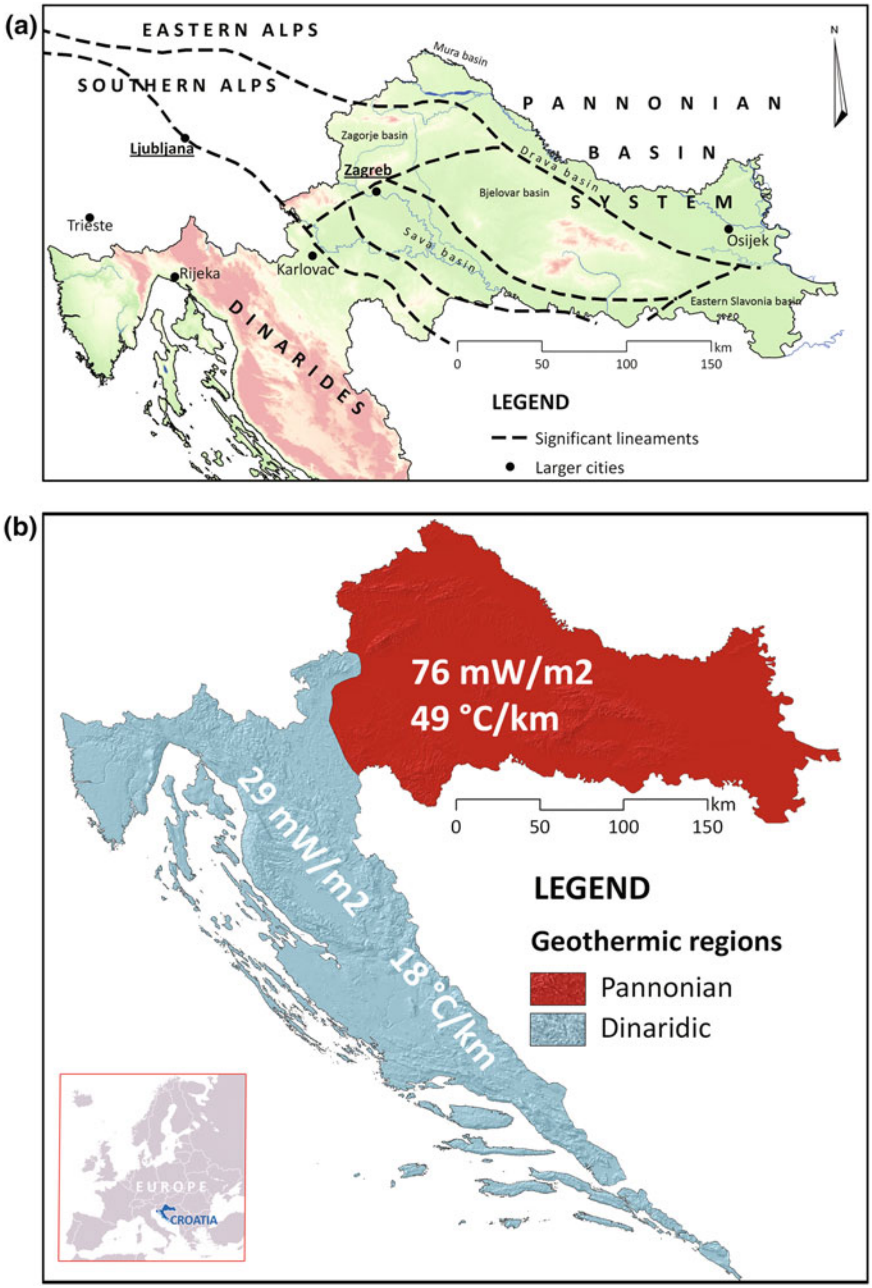

Fig. 1 **a** Position of Croatia in relation to major European tectonic units (according to Tari and Pamić 1998; Lučić et al. 2001; Velić et al. 2012), **b** heat flow density and geothermal gradient in geothermically different Croatian regions

the Dinaric part has low average geothermal gradient (18 °C/km) and surface heat flow (29 mW/m^2) (EIHP 1998).

Differences in geothermal traits are caused by the regional tectonic setting. The Mohorovičić seismic discontinuity (Moho), a boundary between the Earth's crust and mantle, is deepin the Dinarides—50 km, and only 28 km in the Pannonian part (Aljinović and Blašković 1984). Since the mantle convection transports heat more efficiently than conduction in the crust, places where the mantle is closer to the surface will experience higher geothermal heat flow. High values of geothermal parameters in the Pannonian Basin System are a consequence of the middle Miocene (≈16–11.6 Ma b.p.) back-arc extension of the basin, which led to lithosphere thinning and enabled hot asthenosphere to approach the surface (Horváth et al. 2015).

Attempts to explain the occurrence and origin of thermal springs in Croatia date back as far as the 18th century. Many Croatian geologists of those times were studying the warm springs and postulated a number of different hypotheses. Gorjanović-Kramberger (1904) was convinced that thermal springs in north-western Croatia were of volcanic origin, with magma chambers heating the waters and deep faults, *thermal lines*, bringing them to the surface. The main shortcoming of this hypothesis is that there are no recent magmatic bodies to supply heat, but because of Gorjanović-Kramberger's authority it has supporters even today (Šimunić 2008). The idea that thermal waters have meteoric origin, and then get heated during circulation through the underground, first appeared in the works of Pilar (1884). Afterwards, geochemical research of Miholić (1940, 1952, 1959), Horvatinčić et al. (1991, 1996), Marović et al. (1996), Marković and Kovačić (2006), Bituh et al. (2009), Polančec (2011), Kapelj et al. (2014) and Marković et al. (2015) proved that thermal waters of the area are of meteoric origin. As the understanding of the structural fabric of Croatian territory had been advancing, it was proven that the majority of natural thermal springs in the Pannonian part of Croatia are situated in the intersections of anticline crest sand transverse faults (Šimunić and Hećimović 1999). This kind of environment is usually highly fractured and a stark permeability contrast to the surroundings enables the upwelling of heated water from depth to the surface (Caine et al. 1996; Curewitz and Karson 1997; Evans et al. 1997; Faulkner et al. 2010). Water temperature is dependent on the fault dip: if it is vertical, the water loses less heat on the way to the surface, which results in warmer springs. The more the fault deviates from vertical, the more heat is lost on its way to the surface, resulting in ever lower spring temperatures. When the conduits are sub-horizontal, the water can cool down but retains high mineralization and in such cases mineral springs occur (Šimunić 2008).

Mineral and Thermal Water Locations and Categorization

Croatian thermal localities are subdivided into two categories: springs and deep boreholes. Springs are localities where thermal water naturally flowed out or is still flowing out from the aquifer onto the surface. In time, if larger quantities were needed,

Table 1 Categorization of geothermal localities in Croatia on the basis of water temperature (Borović and Marković 2015)

Category	Subthermal	Hypothermal	Homeothermal	Hyperthermal
T (°C)	13–20	>20–34	>34–38	>38
Natural spring	1	6	2	6
Deep borehole	0	4	0	7

intake structures or shallow boreholes were made. At some of those localities natural springs have dried up following higher pumping rates. The category of deep boreholes accounts for all the localities where there are not, nor have there ever been natural springs, and thermal waters were found during hydrocarbon exploration.

Except by the mechanism that they come to the surface, thermal waters also differ in their temperatures. In Croatia they are categorized according to the modified balneological classification (Table 1), created on the basis of traditional Croatian balneological classification which existed since the 1950s (Haramustek et al. 1952), but actually stemmed from considerations of German and Swiss medical balneology experts at the beginning of the 20th century (Jacobj 1907; Hintz and Grünhut 1916; Hartmann 1925).

It is visible that the point of reference for this scale is the average human body temperature, so homeothermal means the same as human temperature (from Greek *homós*—the same), hypothermal is below that temperature (Gr. *hypó*—below) and hyperthermal is above body temperature (Gr. *hypér*—above). The modification was done in the lower part of the scale because in balneology waters with temperatures lower than 20 °C are not considered (Kovačić and Perica 1998). From the hydrogeological point of view, however, all groundwaters with temperatures higher than the average annual temperature of the locality are considered thermal, albeit they cannot be used in balneology. The temperature range in which waters are currently being utilized is from 17 to 98 °C. There are also some deep boreholes which yield waters of higher temperatures.

In Croatia, groundwater is usually characterized as mineral if the total dissolved solids (mineralization) is higher than 1 g/L, or the temperature higher than 20 °C, or contains higher concentrations of a specific dissolved compound that has a strong physiological effect, for example: Fe > 10 mg/L; F > 2 mg/L; J > 1 mg/L; S > 1 mg/L; As > 0.7 mg/L; CO_2 > 1 g/L; Rn > 81.4 Bq/L; Ra > 3.7 Bq/L (Tušar 1998).

Hydrogeochemical Characteristics

A compilation of geochemical data from different sources has been used in this paper to give a general overview of hydrogeochemical characteristics of thermal and mineral waters. It includes chemical analyses by Miholić (1952), Jurišić-Mitrović (2001), Brkić et al. (2007), water quality monitoring of hospitals for medical rehabilitation Varaždinske, Stubičke, Krapinske and Bizovačke Toplice,

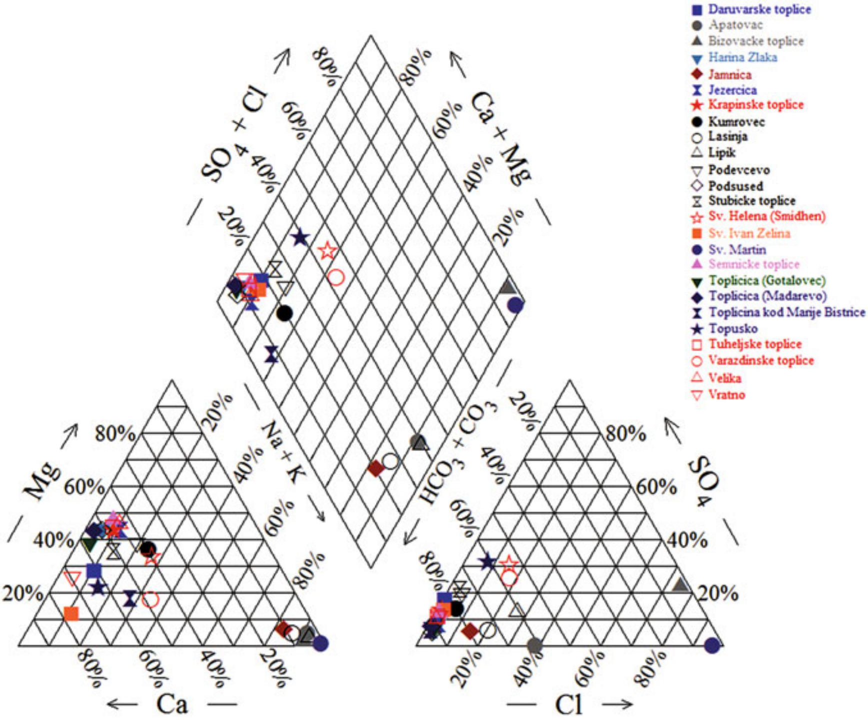

Fig. 2 Piper diagram of selected waters

and chemical analyses performed during research for the Basic Hydrogeological Map, Krapina and Varaždin sheets, in October 2009.

According to the major ionic composition, waters from Varaždinske toplice and Sv. Helena (Šmidhen) belong to a NaCaMg–HCO_3SO_4 mixed type; Podevčevo, Topusko and Stubičke toplice waters belong to a CaMgNa–HCO_3SO_4-mixed-type; Topličina kod Marije Bistrice belongs to a CaMgNa–HCO_3-mixed-type; Harina Zlaka, Tuheljske toplice, Krapinske toplice, Topličica (Mađarevo), Topličica (Gotalovec), Sutinske toplice, Šemničke toplice, Velika, Vratno, Sv. Ivan Zelina, Podsused, Jezerčica, and Daruvarske toplice, belong to the CaMg–HCO_3-mixed-type; Jamnica, Lasinja, Lipik and Apatovac belong to a NaCa–HCO_3-mixed-type and Bizovačke toplice and Sv. Martin waters belong to a Na–Cl-type (Fig. 2). Hydrochemical facies, as recognised from water chemistry data, are a consequence of the chemistry of the recharging water, and water-aquifer matrix interactions, as well as groundwater residence time within the aquifer.

The total dissolved solids (mineralization) are higher than 1000 mg/L (or 1 g/L) in the waters of Lipik, Jamnica, Apatovac, Lasinja, Sv. Martin and Bizovačke toplice (Fig. 3; Table 2). According to the mentioned mineral water classification, they are classified as mineral. Lower mineralization is observed in all other waters and it ranges from 372 mg/L; (Kumrovec) to 963 mg/L (Varaždinske toplice).

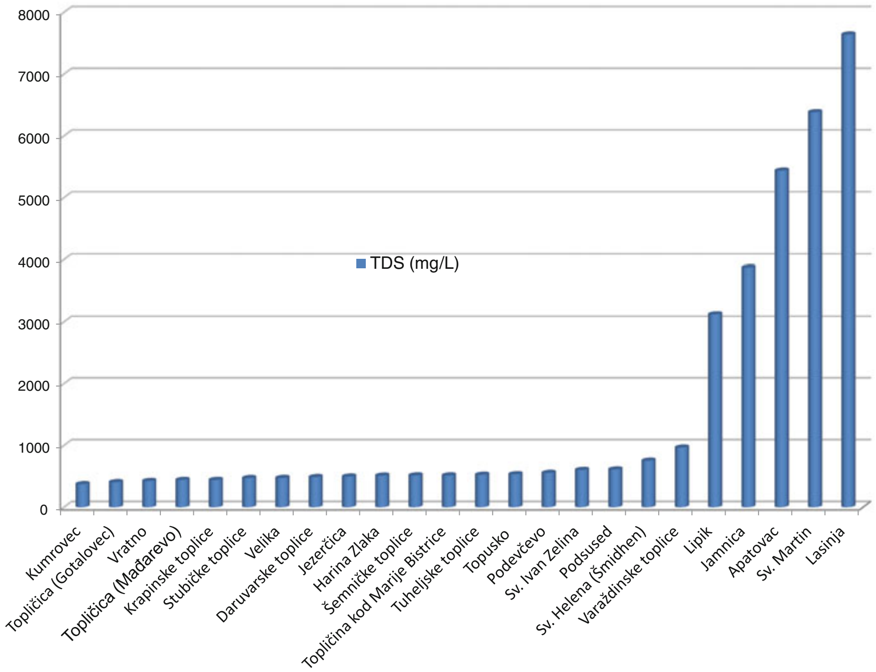

Fig. 3 Distribution of total dissolved solids

From the viewpoint of water temperature, all waters, except the water from Topličina kod Marije Bistrice, are mineral waters because they have temperatures higher than 20 °C (Fig. 4).

Furthermore, water quality monitoring of thermal waters of Varaždinske toplice, Stubičke toplice, Krapinske toplice, Bizovačke toplice and Lipik points to a high content of CO_2, or H_2S, or I^-. In the thermal waters of Varaždinske toplice, a large amount of H_2S (10.4 mg/L) has been observed (Special Hospital 2014). In the waters from Stubičke toplice and Lipik, a high content of CO_2 is registered—101.49 mg/L (Hospital Stubičke Toplice 2014) and 3500 mg/L (Šimunić 2008), respectively. In the waters from Bizovačke toplice and Krapinske toplice, H_2S is also measured (Bizovačke toplice 2014; Hospital Krapinske Toplice 2014). Waters from Bizovačke toplice and Sv. Martin have concentrations of iodide exceeding 1 g/L. Other thermal waters do not exhibit elevated concentrations of specific dissolved compounds.

Waters from Jamnica, Lasinja and Apatovac have a high CO_2 content, with concentrations ranging from 2289 to 3890 mg/L (Šimunić 2008). These waters also have high concentrations of sodium, potassium and chloride; concentrations ranged from 903.9 to 1905 mg/L (Na^+); from 14.6 to 106.8 mg/L (K^+); and from 394.6 to 1011.2 mg/L (Cl^-) (Table 2). The highest concentrations of sodium, potassium and chloride are present in waters from the localities Bizovačke toplice and Sv. Martin (Table 2).

Table 2 Mean values of observed geochemical parameters at localities

	T (°C)	HCO_3^- (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	TDS (mg/L)
Apatovac	12.1	2726.4	54.4	42.4	1583.9	14.6	1011.2	3.1	5436
Bizovačke toplice	90.0	949.3	503.6	79.5	8528.0	226.3	14,750	5926	30,963
Daruvarske toplice	48.2	314.3	77.7	21.7	13.2	3.8	2.0	52.9	486
Harina Zlaka	24.2	362.0	68.7	36.0	7.2	2.3	7.7	25.7	510
Jamnica	12.0	2334.9	106.8	37.7	903.9	106.8	256.8	127.8	3875
Jezerčica	38.4	346.1	58.0	34.0	8.5	15.1	7.8	24.9	494
Krapinske toplice	41.2	298.2	55.3	30.9	10.9	3.1	3.1	38.0	440
Kumrovec	25.0	234.9	40.1	22.4	23.9	7.9	10.6	31.9	372
Lasinja	12.5	4426.0	168.8	57.3	1905.0	76.3	724.1	281	7639
Lipik	52.6	1519.1	30.9	14.7	817.1	91.5	394.6	251.9	3120
Podevčevo	17.7	341.3	58.8	32.8	26.1	9.4	14.3	71.0	554
Podsused	30.5	446.2	82.2	42.5	9.6	1.4	7.8	20.0	610
Stubičke toplice	44.9	284.5	64.8	27.2	16.7	4.3	8.4	64.1	470
Sv. Helena (Šmidhen)	27.3	347.7	83.3	42.5	59.8	7.8	57.0	153.5	752
Sv. Ivan Zelina	21.4	394.5	118.0	11.2	19.3	2.0	7.0	49.7	602
Sv. Martin	36.8	137.0	45.2	15.9	3864.0	98.2	2217	5.0	6382
Šemničke toplice	32.7	355.6	61.5	39.0	9.7	3.0	3.6	40.6	513
Topličica (Gotalovec)	25.6	291.7	60.2	24.8	3.9	2.1	5.2	15.1	403
Topličica (Mađarevo)	23.0	320.1	61.2	29.9	3.3	1.4	3.3	20.5	440
Topličina–Marije Bistrice	17.8	358.2	72.5	14.2	36.3	9.6	4.3	17.9	513
Topusko	47.5	264.6	90.0	19.2	17.9	12.3	19.8	108	532
Tuheljske toplice	32.8	367.9	63.8	36.9	11.3	3.0	3.5	37.6	524
Varaždinske toplice	55.3	450.2	126.1	27.8	82.4	34.6	82.6	159.5	963
Velika	28.2	336.1	53.2	33.5	13.0	1.6	4.2	30.8	472
Vratno	22.0	280.5	83.1	18.8	5.3	2.2	4.0	29.2	423

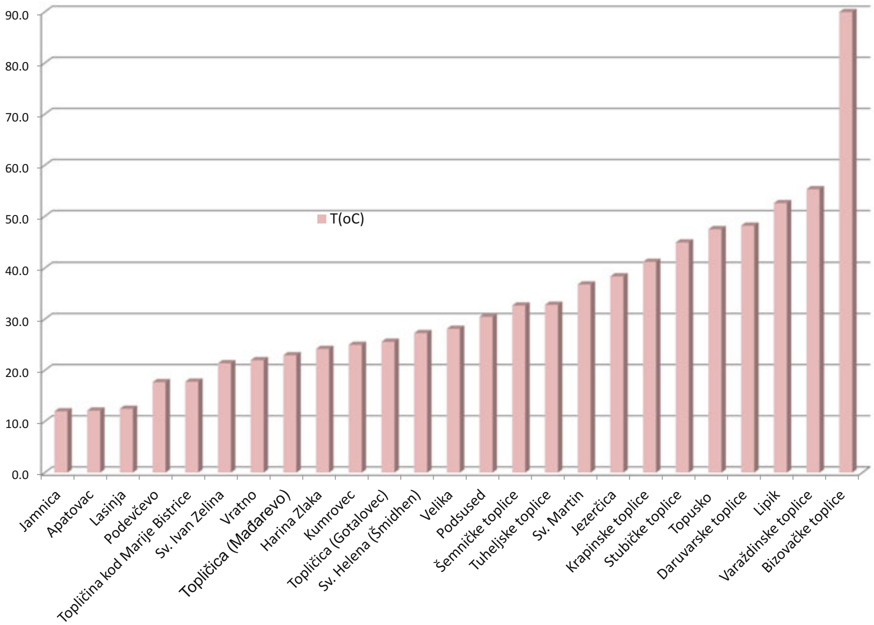

Fig. 4 Distribution of water temperatures

Utilization

The utilized waters considered in this overview range from subthermal to hyperthermal (Fig. 5).

The mode of utilization varies according to temperature, e.g. waters of the lowest temperatures (17–20 °C) are used for fish farming, while waters of the highest temperatures (68–98 °C) are utilized for space heating and hot water preparation. In total, thermal waters in Croatia are utilized in the following ten activities: recreation, balneotherapy, water heating, space heating, greenhouse heating, fish farming and directly as sanitary water, public water supply, and bottled table and mineral water (Table 3).

The most frequent modes of utilization are recreation and balneotherapy, which is the modus known from prehistoric times and antiquity. It is followed by water and space heating and utilization of thermal water for sanitary purposes.

Mineral/thermal waters from the localities Apatovac, Jamnica, Lipik and Topličica (Gotalovec) are utilized for water bottling, and from the localities Harina Zlaka and Vratno for public water supply.

Thermal water utilization in Croatia is stagnating, rather than experiencing growth. Variations in the number of users are mostly the result of temporary closures due to necessary renovation and retrofitting of the outdated infrastructure (Borović and Marković 2015). At some localities where geothermal water is

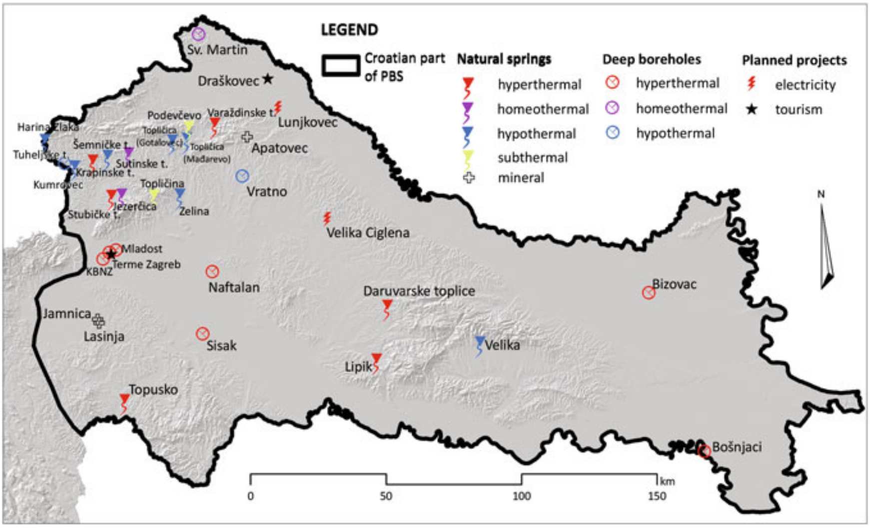

Fig. 5 Locations of thermal and mineral water utilization in the Croatian part of the Pannonian Basin System

Table 3 Geothermal water utilization in Croatia in the year 2014 (Borović and Marković 2015)

Utilization	Type of locality		
	Natural spring	Deep borehole	Total
Recreation	14	3	17
Balneotherapy	7	2	9
Water heating	2	3	5
Space heating	4	4	8
Sanitary water	5	1	6
Fish farming	2	1	3
Greenhouse heating	1	3	4
Table water	0	1	1
Mineral water	1	3	1
Public water-supply	1	1	2

currently being utilized in a single mode, there are plans to increase pumping rates and introduce new modes of utilization since there is a consensus that having more users and extracting as much heat as possible significantly increases economic viability of thermal projects (Rybach 2003; Legmann 2003; Lund et al. 2005; Pravica et al. 2006). The most diversified use is accounted for in Stubičke toplice (Fig. 5): recreation, balneotherapy, water and space heating, greenhouse heating and sanitary water.

Other than improving heat extraction at active locations, significant interest is present to utilize thermal waters and/or energy in new locations (Borović and Marković 2015). The projects in higher stages of development include Terme Zagreb (using a set of existing boreholes) and Draškovec (Međimurje County in the north of Croatia) (Fig. 5). For all the mentioned localities, the plan is to utilize thermal waters in cascade systems for facility heating, hot water preparation, spa and recreation, greenhouse heating and/or fish farming, to make the process economically feasible.

Borović and Marković (2015) clearly show that the potential of geothermal electricity generation in Croatia could not supply a significant portion of the country's electricity demands. It is considered marginally profitable, depending on the project, because available resources have temperatures up to 170 °C, i.e. low enthalpy sources, which are used for the less economical binary process (Kristmannsdóttir and Ármannsson 2003). The most significant potential for power generation was identified in Velika Ciglena and Lunjkovec (Fig. 5). According to the Croatian National Renewable Energy Action Plan (Ministry of Economy 2014), the first geothermal power plant Marija-1 (4.71 MW_e) is supposed to start operation in the year 2016 in Velika Ciglena. The projects also include cascade utilization of thermal water to make the schemes economically viable.

The Croatian heating and cooling sector could benefit greatly from large scale geothermal utilization, since full development of the existing fields could supply over 13 % of the energy demand, excluding geothermal heat pump utilization (Borović and Marković 2015). There are 3500 boreholes in the Pannonian part of Croatia, leftover from hydrocarbon exploration and exploitation, many of which represent an untapped local energy micro potential (Kolbah and Škrlec 2010). The idea of utilizing these boreholes is neither new, nor unexpected. It has been determined that significant energy potential is present in the water surrounding mature hydrocarbon extraction sites with deep boreholes, high temperatures and favourable permeability conditions, which could be retrofitted for geothermal water extraction during and after hydrocarbon exploitation (Čubrić 1978; Kurevija and Vulin 2011). One of the obstacles for stronger integration of geothermal energy into the heating sector is the fact that the same region rich in geothermal potential also has a developed gas pipeline network. Natural gas heating is a strong competitor because it is readily available, while geothermal boreholes are often a few kilometres away from settlements, so it would be necessary to build insulated hot water pipelines, which is very costly (Čubrić 1993; Fridleifsson 2003; Szita 2015). In this situation, even when awareness of possible renewable resource utilization exists, it succumbs to economic interests.

Sustainability and Environmental Impacts of Thermal Water Utilization

The need for protection was actually the very thing that prompted early research of geothermal springs in Croatian territory, after the Croatian parliament passed the law on "*Protection of curative and mineral baths*" in 1885. Protection zones around the springs were quite extensive and there are multiple court disputes over possibilities of private land management and digging of drinking water wells in protective zones conserved in documentation of that time (Šimunić 2008). Scientists and the authorities were obviously aware of the potential danger that nearby boreholes could present to natural springs. Geological research has since demonstrated that recharge of geothermal aquifers, which feed the springs, occurs in mountainous hinterlands of the springs (Šimunić and Hećimović 1999). This means that the danger to such springs comes also in the form of forestry activities and large quarries. The utilisation of explosives is particularly dangerous because it creates seismic events that can impair hydraulic properties of both the aquifer and the discharge area. The troubling fact is that the dominant geothermal aquifers in Croatia are Triassic dolomites which are also being mined in 17 active quarries in the Pannonian part of the country (Živković and Krasić 2008). There were many reports from Sutinske toplice (Fig. 5) that mining in the nearby dolomite quarry has the same impacts as natural earthquakes, i.e. changes in yield of the springs. More drastic was the example from nearby Šemničke toplice (Fig. 5), where the spring did actually dry up after intensive mining in the same quarry, only to reappear after a longer period of time, but in two new locations (Šimunić 2008).

Waters from deep confined aquifers discovered during hydrocarbon exploration are not a part of the contemporary hydrologic cycle, meaning they are devoid of any significant recharge and can only be utilized in a sustainable manner by production–reinjection doublets (Eckstein and Eckstein 2005). Aside from that, their quality can be reduced by oilfield waste disposal in the boreholes, which has become a frequent practice (Šimunić 2008).

Discussion and Concluding Remarks

Favourable geothermal properties, which are characteristic of the major part of the Pannonian Basin System, also extend into its south-western margin where Croatia is situated. Owing to a thin lithosphere, geothermal heat flow is high and enables groundwater to heat up. Some of the natural geothermal springs have a millennial tradition in different modes of utilization. In the 20th century new thermal and mineral water resources were identified during hydrocarbon prospecting. According to temperature, thermal waters are predominantly hypothermal and hyperthermal, both at natural springs and boreholes. The majority of thermal waters have low mineralization and a low CO_2/H_2S content and they can be utilized as potable water, which is already the case at some locations. Others have high mineralization and a high CO_2/H_2S content. Mineral waters have high dissolved CO_2 and a high content of sodium, potassium, and chloride. The type of thermal and mineral water occurrence and the modes of utilization dictate the potential problems that did or could arise. In the Croatian example, the vulnerability of utilized sources of geothermal water to qualitative and quantitative status deterioration differs among natural springs fed by hydrothermal systems and waters from deep boreholes, since the former are part of the contemporary hydrologic cycle, while the latter are not. In accordance with their characteristics, natural springs are mainly endangered by forestry and quarries, while waters from deep boreholes are at risk of contamination by fluid waste disposal. Despite significant potential confirmed through multiple professional and scientific studies, the utilization of both thermal and mineral waters remains at low levels and traditional applications.

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Thermal Waters in Bulgaria

Aleksey Benderev, Vladimir Hristov, Klara Bojadgieva and Boyka Mihailova

Abstract The geological structure of Bulgaria is a complex mosaic of plates and orogenic structures, characterized by deep faulting and lithofacial and magmatic contrasts. Three types of reservoirs are found in the country: stratified (northern Bulgaria), fractured, and mixed, where mineral water from a fractured reservoir is secondarily accumulated in a younger sediment reservoir (southern Bulgaria). The water temperature of all discovered geothermal reservoirs ranges between 25 and 100 °C, while those with temperatures up to 50 °C prevail. The flow rate varies from 1 to 20 L/s in about 75 % of the reservoirs. The established chemical content (TDS) is in the range from 0.1 to 1.0 g/L in southern Bulgaria and 0.1 g/L (100–150) g/L in northern Bulgaria. About 70 % of the discovered thermal waters are slightly mineralized (less than 1 g/L) and suitable for drinking. Direct thermal water application has an ancient tradition in Bulgaria. Current uses include balneotherapy, space heating and air-conditioning, greenhouses, thermal water supply, ground source heat pumps (GSHP), bottling of potable water and soft drinks. The present installed thermal capacity amounts to about 83.1 MWt, excluding GSHP. An extensive review of the geological background, thermal water characteristics and existing applications is presented. Thermal waters are an integral part of Bulgaria's total water resources but due to their particular qualities, they are treated separately by legislation. Water management and legislation are briefly presented.

Keywords Water resource · Hydrothermal regions · Thermal water · Application and legislation · Bulgaria

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A. Benderev (✉) · V. Hristov · K. Bojadgieva · B. Mihailova
Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. Bl. 24,
1113 Sofia, Bulgaria
e-mail: alekseybenderev@yahoo.com

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Introduction

Bulgaria is situated in the southern part of the Balkan Peninsula (Fig. 1). Its total land area is 110,994 km^2 and it has a population of 7,364,570 according to the 2011 national census.

Water resources are relatively sparse and unevenly distributed across the territory of the country. The water balance is formed by limited rainfall, intensive evaporation, prevailing surface river flow and low quantitative accumulation on the territory. Total evaporation varies significantly, as a percentage of precipitation, from 46 to 89 %.

Bulgaria is among the last countries in Europe with regard to annual water availability per capita. It amounts to about 2,600 m^3, including both internal resources and contributions from other countries (Nyagolov et al. 2012). However, nearly all water resources are formed within Bulgarian territory, which makes it less dependent on waters flowing across the borders. Rivers, dams and groundwater (especially thermal) are of the greatest economic importance to Bulgaria. The share of groundwater is about 20–30 % of all water resources. The water supply is predominantly 70 % from surface water and 30 % from groundwater.

The average annual water volume is estimated at 17.5 × 10^6 m^3, in the period 1961–2008 (Nyagolov et al. 2012). Rivers have the largest share in the structure of water resources. Their regime is formed primarily by the moderate continental and continental–Mediterranean climate of the country. The Balkan mountain (Stara Planina) divides the country into two parts (northern and southern), stretching from the west to the east, across the territory. Almost all river systems in northern Bulgaria have their beginnings there. In a number of hydrological basins groundwater originates mainly from infiltration of river flow.

The growing need for drinking water and use of renewable energy sources require better knowledge and management of groundwaters, especially thermal waters. The capital of Bulgaria—Sofia is one of the three capitals in Europe, along with Reykjavik (Iceland) and Budapest (Hungary), which was formed around thermal water sources in ancient times.

Fig. 1 Location map

Thermal waters are classified as part of mineral waters in Bulgaria. According to the Water Act, mineral waters are those that have a beneficial physiological effect on the human body through dissolved salts, gases and heat contained in them. Mineral waters are grouped in terms of temperature: hypothermal (cold), with temperatures up to 25 °C; warm, with temperatures from 25 to 37 °C; and hot, greater than 37 °C. Cold mineral water sources are scattered throughout the country. Mineral waters with temperatures above 25 °C are considered as thermal. They constitute the majority of mineral waters in Bulgaria.

Bulgaria's mineral and thermal waters have been subject to exploration and exploitation since ancient times. There are numerous publications on the exploration of hydrothermal sources and systems, as well as analyses of various aspects of thermal water use in the country: Radev (1930), Azmanov (1940), Kusitaseva and Melamed (1958), Shterev (1964, 1970), Petrov et al. (1970), Marinov et al. (1971), Petrov (1964, 1973), Velinov and Bojadgieva (1981), Shterev and Penev (1991), Gasharov and Bojadgieva (1993), Hristov (1993), Shterev and Zagorchev (1996), Vladeva and Kostadnov (1996), Pentcheva et al. (1997), Fournadzieva et al. (2002), Shterev (1977, 2002), Fournadzieva and Bojadgieva (2004), Hristov et al. (2000a, b, 2010), Hristov and Bojadgieva (2003), Bojadgieva et al. (1992, 2002, 2010a, b, 2015), and others.

To date, about 250 hydrothermal fields and occurrences have been discovered on Bulgarian territory. According to the Water Act, 102 of them are specified as exclusive state property. The rest are municipal property.

The aim of this review is to present an extensive analysis of the hydrogeological conditions in the country, the physical and chemical properties of thermal waters, existing uses, and possibilities for future development of this energy sector.

Geological Background

Rocks of different origin, various lithologic and petrologic compositions, varying from Precambrian to Quaternary in age, have built up the territory of the country (Yovchev 1971; Dabovski et al. 2002; Zagorchev 2009). The territory of Bulgaria covers parts of two major tectonic units: the northern part of the Alpine thrust belt in the Balkans, and its foreland—the Moesian platform (Zagorcev 1992; Zagortchev 1994). The Alpine thrust belt is divided into two orogenic systems: the South Carpathian system, which is poorly exposed in the northwestern corner of Bulgaria, and the Balkan system, subdivided into three main zones (Balkan, Sredna Gora, and part of Moravia–Rhodope zone, named Rila–Rhodope massif) (Fig. 2). The Moesian platform is located in both Bulgarian and Romanian territory. The platform has a Caledonian–Hercynian basement and a cover of Upper Paleozoic and Mesozoic sediments. In the Bulgarian part, their thickness decreases from about 6 to 7 km in the west to several hundred meters in the east. Up to 1000 m thick artesian aquifers built up of limestone and dolomite, very fractured and with high permeability, are found in the plate.

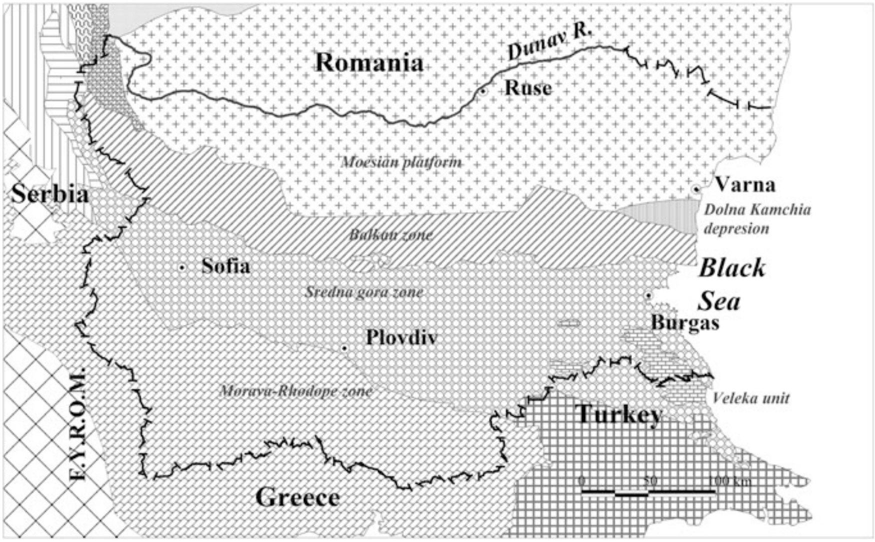

Fig. 2 Tectonic map of Bulgaria (after Zagorcev 1992)

Metamorphic and magmatic complexes are mainly spread in the three folded tectonic units: Balkan zone, Sredna Gora zone and Rila–Rhodope massif. Geothermal waters are predominantly formed in granites and gneiss (Fig. 3).

The Balkan Zone is presented by Alpine structural complexes (Yovchev 1971). The Sredna Gora Zone is bounded by the Balkan mountain to the north and by the Maritsa fault to the south. The wide development of the Pre-Alpine structural complexes that have been split by enormous Caledonian–Hercynian granitoid batholiths is typical of this zone. The Rila–Rhodope massif consists of four structural complexes: Archaic, Proterozoic, Caledonian–Hercynian and Alpine. The foundation of the massif is formed by pre-Cambrian complexes and by the Caledonian Structural Stage of granitic rocks in the West Rhodope Block. The second important stage in the formation of the massif occurred in the young-Alpine age, when depressions with thick volcanogenic–sedimentogenic deposits were formed.

Thermal Field

Thermal field distribution depends on three major factors: geological structure, tectonic development and hydrogeological activity.

The temperature distribution at different depth levels is associated with thick Mesozoic and Neozoic sediments of the Moesian platform, which act as heat

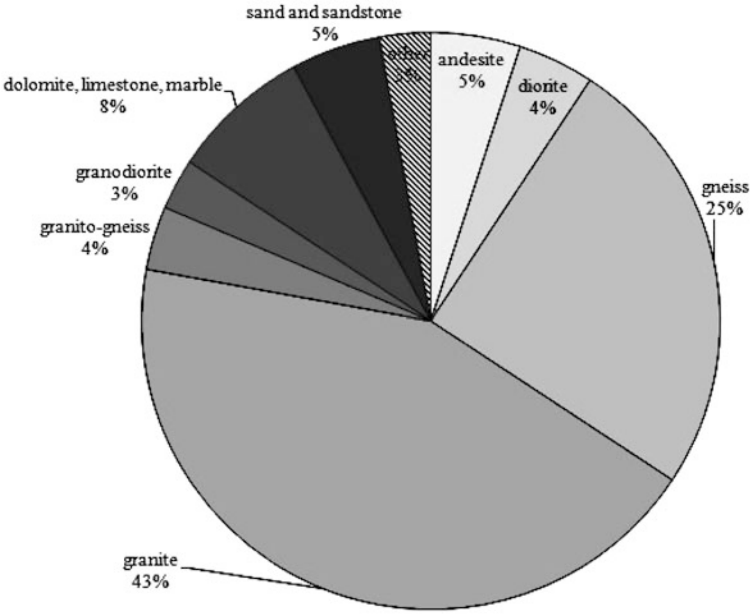

Fig. 3 Reservoir rocks in southern Bulgaria

accumulators, and the strongly fractured and denivelated Paleozoic basement. The outlined temperature anomaly (50 °C) in the western part of northern Bulgaria is associated with a thick (up to 7 km), dense, terrigenous–carbonate cover (Fig. 4). Its thickness gradually decreases to several hundred meters in the easterly direction. The lithology also changes in the same direction. Stratified reservoirs are typical of the Moesian platform and are associated with carbonate strata of Senonian, Upper Jurassic/Lower Cretaceous, Middle Triassic and Upper Devonian ages. The Upper Jurassic/Lower Cretaceous aquifer is widespread on the entire territory of northern Bulgaria. In the western part it is deep-seated (up to 3.6 km), featuring the highest thickness (1000 m) and low filtration properties. Further to the east, the depth of deposition and thickness decrease; in the north–eastern part it outcrops at some points and then the aquifer sinks steeply to the Black Sea. The aquifer becomes more permeable in the central part and along the Black Sea coast, where it creates positive temperature anomalies. The lowest temperature values are registered in the north–eastern part (between 20 and 25 °C), cooled down by the circulation of cold water in the aquifer recharge zone.

Contrasting geothermal conditions in southern Bulgaria are associated with high mountainous horsts and deep intermountainous grabens occupied by numerous Paleogene and Neogene sedimentary basins. The high mountains have a strongly segmented relief and represent open hydrological systems with low temperatures. Ascending confined thermal waters have created large positive anomalies with high

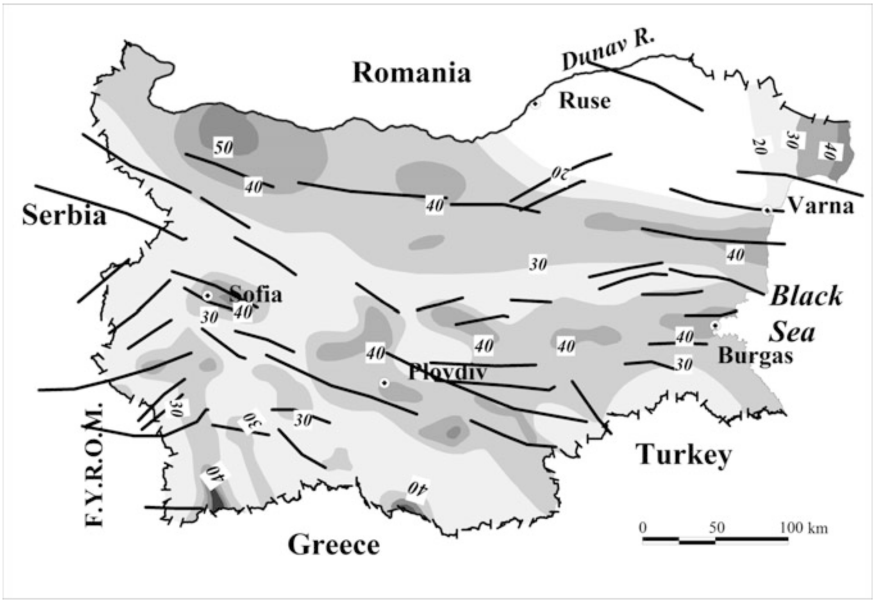

Fig. 4 Seismic activity zones (after Kastelic et al. 2011) and temperature distribution at 500 m below the surface (after Bojadgieva et al. 2001)

temperatures and geothermal gradients. The registered temperature anomalies are mainly associated with hydrothermal fields and neotectonic activity (Fig. 4). Temperature isolines are predominantly oriented in NW–SE and W–E directions, like the active neotectonic faults and main geomorphological structures. The three temperature anomalies in the south–western part, with approximately NW–SE orientation, are formed by hydrothermal fields located along old faults.

Hydrothermal Regions

Hydrothermal regions are closely linked to the main geological structures. The deep hydrogeological division of the country is a mosaic of macro- and mega-hydrothermal systems. They form three major hydrogeological regions: Low Danubian Artesian, Intermediate, and Rila–Rhodope (Fig. 5). The Intermediate and Rila–Rhodope regions are characterized by greater discovered water quantities and more diverse application compared to the Low Danubian Artesian region.

Three types of reservoirs are found in the country: stratified, fractured and mixed (water from a fractured reservoir is secondarily accumulated in a younger sediment reservoir).

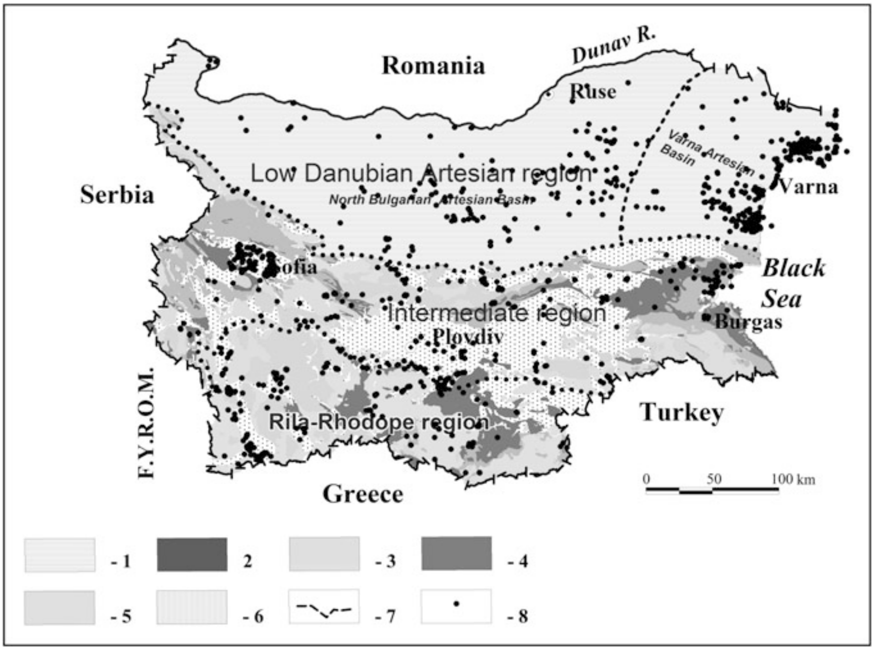

Fig. 5 Main hydrogeological regions in Bulgaria and hydrothermal sources distribution *1*—layered type aquifers; *2*—intrusive rocks with fractured type water; *3*—highly crystalline metamorphic rocks with fractured type water; *4*—effusive and volcano-sediment rocks with fractured and layered-fractured type water; *5*—sediment rocks with fractured and karst type water; *6*—unconsolidated Quaternary-Neogene sediments with porous type water; *7*—boundaries between main hydrogeological regions; *8*—thermal water sources and occurrences

The main geothermal reservoirs in the Low Danubian Artesian region are developed in carbonate strata. The Intermediate region is characterized by unstratifed (fault-fractured), stratified and mixed hydrothermal systems. Water circulation takes place in the fractured massif of granite and metamorphic rocks and in Upper Cretaceous volcano–sedimentary deposits. Hydrothermal reservoirs are also formed in many postorogenic Neogene–Quaternary grabens (depressions), filled up with terrigenous deposits. Only the western part of the Rila–Rhodope massif is rich in thermal water. It is built of Precambrian metamorphic and granite rocks, fractured by a dense set of seismically active faults. Unstratified hydrothermal systems with thermal waters of low salinity, meteoric origin and temperatures up to 100 °C are found in this area. The metamorphic basin contains some large bodies of marble that act as hydrothermal reservoirs. Permeable terrigenous–clastic rocks in the deep Neogene and Paleogene grabens also contain thermal waters. Most of the discovered sources there are associated with tectonically active zones. Water reservoirs are predominantly formed at the crossing zones of the lineaments.

Thermal Water Characteristics

The basis for resource assessment is data taken from about 250 hydrothermal fields and occurrences located all over the country. Data from different sources—natural springs, wells, and galleries, have been summarized and analyzed. As a rule, wells in northern Bulgaria are deeper than those in southern Bulgaria. The depth of the wells reached about 5000 m in the northern part and up to 2000 m in the southern part (Bojadgieva and Gasharov 2001).

Temperature and Flow Rate

Water temperature and flow rate distributions in Bulgaria are shown in Fig. 6. The highest temperature (98 °C) is measured in Sapareva banya town (southern Bulgaria). The highest flow rate, which could technically be used, is concentrated in the Upper Jurassic–Lower Cretaceous aquifer (NE Bulgaria)—1039 L/s, and in the Chepino basin—145 L/s (SW Bulgaria) (Ministry of Environment and Water 2015).

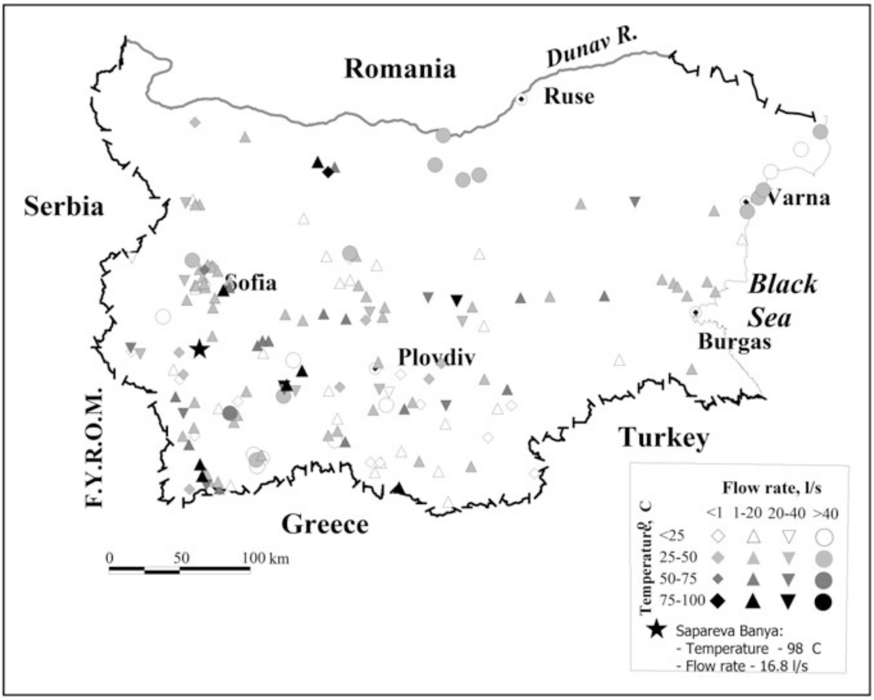

Fig. 6 Temperature and flow rate distribution of hydrothermal fields

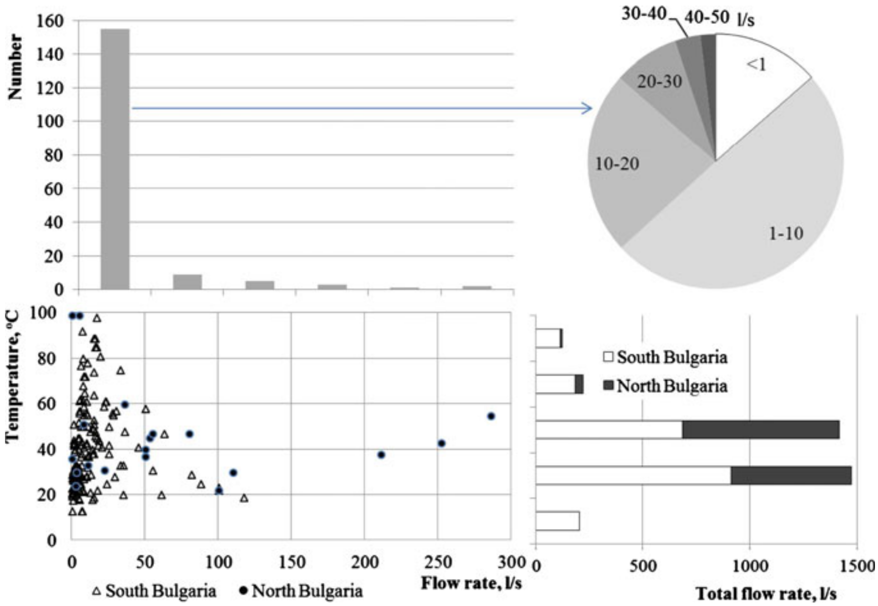

Fig. 7 Summarized presentation of temperature and flow rate data

Summarized information on the temperature range and flow rate values for both northern and southern Bulgaria and the number of hydrothermal reservoirs falling in different flow rate intervals are presented in Fig. 7.

The water temperature of all discovered hydrothermal fields in Bulgaria ranges between 25 and 100 °C, where the number of fields whose temperatures are between 25 and 50 °C is dominant. Only nine fields have temperatures higher than 75 °C and the total flow rate in each of them varies between 13 and 23 L/s. Temperatures and discovered water quantities in the southern part are higher than in the northern part.

Several chemical geothermometers (chalcedony, Na/K, Na/Li, Na/K/Ca, K/Mg) have been used to predict reservoir temperatures of some hydrothermal fields in Bulgaria (Veldeman 1991; Hristov 1993; Pentcheva et al. 1997). The chalcedony geothermometer proved to be the most appropriate to indicate reservoir temperature, according to the obtained results. The highest predicted temperature is for the hydrothermal field at the site of Draginovo (156 °C) (Chepino basin, southern Bulgaria). Temperatures of about 150 °C are also expected in the deeper-seated sedimentary reservoirs of Devonian and Triassic age in the Moesian platform (northern Bulgaria) and in Sapareva banya and Chepino basin (southern Bulgaria) (Hristov et al. 2003).

The maximum predicted temperatures at the other sites in the country are in the 100–110 °C range. The possibilities of discovering geothermal water with significantly higher temperatures than registered at present are small. Most of the samples represented mixed ground waters or non-equilibrium waters and that resulted in unrealistic predicted temperatures. The data obtained from applied chemical geothermometers show that the geothermal fields in Bulgaria could be characterized as "low temperatures". The hydrothermal fields in southern Bulgaria—Draginovo, Blagoevgrad, Pchelin banya and Sandanski, are expected to be the most promising with respect to geothermal potential (Hristov 1993).

The total dynamic flow rate of sub-thermal and thermal waters goes up to 4600 L/s (Petrov et al. 1998), of which about 3000 L/s is the flow rate of the revealed thermal waters of $t > 25$ °C. The exploitable part of the resources did not significantly change in the period 2004–2014, varying between 25 and 28 %. New drilling could discover about 2300 L/s of recoverable resource in addition (Petrov et al. 1998). The majority of the Bulgarian hydrothermal fields have a total flow rate between 1 and 20 L/s (Fig. 7).

More efficient use of hydrothermal resources is possible through reinjection. Most suitable for this purpose are aquifers in the Lower Danubian Artesian region as well as in the Sofia Valley (Intermediate region).

Chemical Composition

Different geological and tectonic environments in northern and southern Bulgaria determine a wide variety of chemical compositions and gas content of the water. Some of the main factors controlling water formation are the depth and lithological structure of the aquifer, and the distance from the recharge zone.

Data from chemical analyses of aquifers in northern Bulgaria have been published by Yovchev and Rijova (1962) and Monahova (1964, 1972, 1975), and in southern Bulgaria by Pentcheva et al. (1997), Vladeva and Kostadinov (1996), Vladeva et al. (2000) and others. The aquifers in the Low Danubian Artesian region have been studied mainly in connection with prospecting and exploration of oil and gas. The total dissolved solids (TDS) in northern Bulgaria vary from less than 1.0 g/L in shallow aquifers to more than 150.0 g/L in aquifers located at a depth of about 6.0 km. The TDS increase with depth is clearly registered in the Upper Jurassic–Lower Cretaceous aquifer, which is spread across the territory of northern Bulgaria. In parallel with TDS increase, the water type changes from HCO_3–Ca and HCO_3–Ca–Mg to Cl–Na.

The concentrations of J, Br, B, and Sr in northern Bulgaria are higher in the north–western and south–eastern parts, where their extraction becomes economically feasible. Nitrogen (N_2) dominates in shallow parts and decreases with depth. CO_2 and H_2S concentrations increase with depth, as do hydrocarbons, predominantly methane in the case of a stagnant water regime.

The chemical composition of groundwater in southern Bulgaria is rather different from that in northern Bulgaria. Data analysis is based on the analytical results of sampling from natural geothermal springs and wells. More than 90 % of them have a low TDS (below 1.0 g/L), although they occur in different geological media

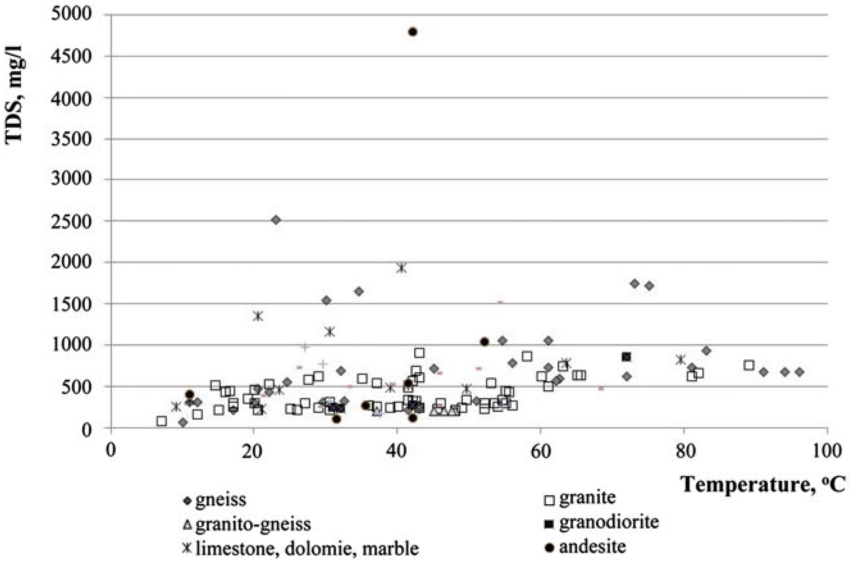

Fig. 8 Total dissolved solids versus water temperature for various lithological types

(volcanic, intrusive and metamorphic rocks) (Fig. 8). Only several water samples from sedimentary rocks show TDS values up to 5.0 g/L, as do mixed waters sampled near the seashore. Waters with higher TDS values are accumulated in carbonate rocks, gneiss or volcanic rocks.

Generally, most geothermal waters in southern Bulgaria are N_2-bearing, alkaline (pH up to 10.5), fluoridic, often radioactive and containing reduced sulfur species. They are always sodium-bearing, poor in magnesium, predominantly HCO_3–Na; HCO_3–SO_4–Na and SO_4–Na. The waters are rich in dissolved and spontaneous helium and have specific micro compositions: Li, Rb, Cs, W, Ge, Ga, Mo and Be (Pentcheva et al. 1997). The prevailing low TDS values enable widespread use for bottling of potable water and direct supply for everyday necessities.

Carbon dioxide waters have been discovered in a few sites: Mihalkovo, Stefan Karadzhovo, Rupite, etc. Hydrogen sulfide thermal waters are found in Sofia Valley. Half of the thermal waters exhibit elevated radioactivity, from 50 to 4500 Bq/L.

Thermal Water Application

The major factors promoting geothermal development in Bulgaria are long tradition, favorable climate, appropriate thermal water composition and a developed spa system. Many Neolithic and Paleolithic settlements (5–6 thousand years BC) were

Fig. 9 Remains of Roman bath complex in Hissarya town (S. Bulgaria)

based around hot springs, nowadays Sofia city, Kyustendil town, Stara Zagora town and others. This process continued during the settlement of Thracians, Greeks, Romans, Byzantines, Slavs, Turks and Bulgarians. Remains of ancient buildings and bathing facilities have been discovered in over 25 settlements (Bojadgieva and Hristov 2006) (Figs. 9 and 10). Thermal water application was most extensive at the time of the Roman Empire. Many public baths, clinics (asclepions) and shrines (nympheums) were built in honor of the ancient gods Aesculapius, Hygeia and Heracles. Roman Baths in Varna (Odessos) (2nd/3rd century AC) constitute the largest complex discovered in the country so far.

In spite of a good hydrothermal capacity of 9957 TJ/year (Petrov et al. 1998), the application of thermal waters is still limited. The exploitable part of the discovered quantity is currently about 28 %, of which 4 % is utilized under a concession regime (mainly for bottling of mineral water) and 24 % is available to users for all other applications, through permits (Ministry of Environment and Water 2015). The installed thermal capacity (2014) amounts to about 83.1 MWt, excluding GSHP (Bojadgieva et al. 2015).

Due to the relatively low temperatures (below 100 °C), thermal waters only have a direct application. The variety of uses nowadays includes: balneotherapy (prevention, treatment and rehabilitation, bathing and swimming pools), space heating and air-conditioning, greenhouses, geothermal ground source heat pumps, direct thermal water supply, bottling of potable water and soft drinks (Fig. 11).

Fig. 10 Remains of Turkish bath in Sofia city

The Water Act defines three categories of thermal water utilization: water supply (when no alternative is available), treatment and rehabilitation in specialized medical centers, and a combination of all other applications (balneotherapy and energy). The fees for water use are defined according to the three categories. They vary according to temperature and are the lowest for water supply (Bojadgieva et al. 2015).

Present leading applications in terms of water quantity are in balneotherapy and direct thermal water supply. Utilized water for relaxation and sanitary needs has the highest share in balneotherapy due to intensive application in spa hotels located in mountain and seaside resorts. Extremely good bio-climatic resources, combined with Mediterranean traditions in thermal water use, provide a basis for successful balneological activity in the country.

Direct supply with mineral water is typical of several resorts along the northern Black Sea coast: Golden Sands, Albena, Kavarna and Balchik. Drinking mineral water from taps in spa resorts is free of charge.

The share of water used for space heating, air-conditioning and greenhouses is small and accounts for a total of 3.6 % (Bojadgieva et al. 2015). Heating is provided only to individual buildings not connected to a district heating system. Heating installations are assisted by plate heat exchangers. In addition, they prepare domestic hot water and are in operation for about 200 days/year. The greenhouses cover an approximate area of 10 ha and produce vegetables and flowers for the local market.

About 20 bottling plants are currently in operation. This activity is regulated by the Law on Concessions. There are several major reasons for the development of bottling, including: predominant thermal waters of low TDS (<1 g/L); a wide variety of chemical compositions that provides an opportunity for bottling of potable water as well as of mineral water for drinking in prescribed doses; and short-term payback period. Production mainly meets the demand of the local market. Geothermal ground source heat pumps (GSHP) show significant progress but officially summarized information is still unavailable. Water uses for clothes driers and washers, technological needs of different enterprises (oil, food and soft drinks production), and plant irrigation also exist but have a small share of about 3 % (Bojadgieva et al. 2015).

Presently, only seven of 28 administrative districts have no utilization. Geothermal activity is mainly concentrated in the southern part of the country due to the high water temperatures there and low water salinity (TDS), mostly below 1 g/L. The hydrothermal basins that play a leading role in water application are Razlog, (southern Bulgaria), southern Sredna Gora, Chepino, Struma and the region of NE Bulgaria (Fig. 11). They account for 47 % of all hydrothermal resources in use. Intensive construction in mountainous, coastal and rural regions over the past 25 years has prompted more effective or complete thermal water application in some areas.

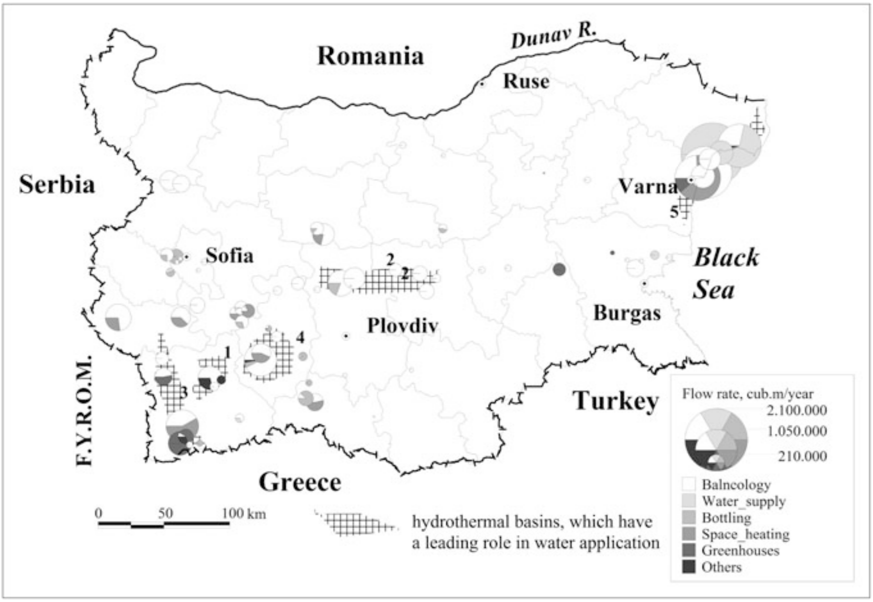

Fig. 11 Geothermal application in administrative districts (towards 2010). *1* Razlog, *2* Southern Sredna Gora, *3* Struma, *4* Chepino, *5* NE Bulgaria

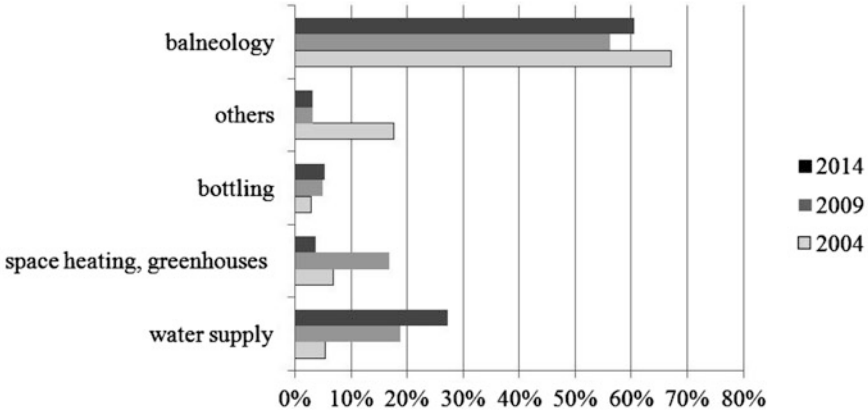

Fig. 12 Thermal water use within 10 years period

The 2004–2014 trend of the direct use of thermal water is shown in Fig. 12. Space heating and greenhouse development have been declining, while balneotherapy (bathing and swimming) showed progress over the entire ten year period. Thermal water is currently used for space heating and domestic hot water in only a few balneological sites. Many old heating installations in poor technical condition have been shut down and only a small number of new installations constructed. The total installed capacity decreased after 2004 by 29 % and remained almost unchanged between 2009 and 2014.

Administration and Legislation

Until 1990, geothermal heating systems were entirely financed by the state. Bulgaria has no specific legislation for geothermal energy. Regulations exist, however, for obtaining permits and concessions for thermal water use, and there are guidelines in place for geothermal exploration. Thermal waters are an integral part of the total water resources in Bulgaria but due to their particular qualities they are treated separately by the legislation.

According to the Water Law (1999), thermal waters are owned by the state or by municipalities. The Ministry of Environment and Water (MOEW) approves exploitable thermal water resources and hydrothermal energy, and designates wellhead protection zones of all reservoirs (state-owned and municipal). The Ministry of Health monitors the mineral composition and the general state of all water sources.

State-owned thermal waters are administered by the Council of Ministers, according to the Concession Law (1995), through a concession regime, and by the MOEW—according to the Water Law (1995), through permits. Municipalities manage local thermal waters according to the Municipal Property Law (1996).

Some promotional steps have recently been taken, like alleviating administrative regulations, reducing fees for thermal water use, and normatively requiring cascade systems of exploitation. According to the latest amendments to the Water Act, about 70 state-owned fields have been identified for granting to the municipalities for a period of 25 years. Thermal waters could be administrated on the spot by legal entities and individuals.

The main barriers for thermal water use are mainly related to the lack of: administrative capacity and funds of the municipalities for water management; state support needed to improve the poor condition of the water sources granted to communities and to provide further studies for resource assessment; and local investment interest and strategic partners.

Conclusions

The low-enthalpy hydrothermal resources in the country have potential for future development as direct application. The existing know-how in geothermal energy use for space heating and air-conditioning, combined with the new administrative regulations, will provide better conditions for the utilization of these renewable sources. The application of ground source heat pumps will likely continue to grow and balneotherapy will preserve its leading role. The legislative changes are expected to attract greater interest in more sustainable thermal water utilization.

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Mineral Waters of Montenegro

Mihailo Burić, Zoran Nikić and Petar Papić

Abstract Mineral water resources, and especially thermal water resources, are relatively sparse in Montenegro. This is a result of the specific geological makeup and complex tectonic relationships. However, due to insufficient insight into the origin of these water resources, particularly the hydrogeological conditions, as well as geochemical relationships, as surveys in this area have been relatively modest in terms of both extent and scope, no optimal results have been achieved that would enable the utilization of these water resources for useful purposes. Mineral and thermal waters are found in three hydrogeological zones of Montenegro: coastal, central and Inner Dinarides. Five types of mineral water are allocated on the basis of hydrochemical characteristics: Na–Cl; Ca–HCO_3; Mg, Ca–HCO_3 with CO_2; Na, Ca–HCO_3 with CO_2 and Na–HCO_3, Cl with CO_2.

Keywords Mineral water · CO_2-rich water · Thermal waters · Hydrogeological zones · Montenegro

Introduction

The Republic of Montenegro occupies a land area of 13,812 km^2. According to the 2011 census, the population is 620,029. Geographically, it is situated in the western part of the Balkan Peninsula. It borders on Serbia to the northeast, Bosnia and Herzegovina and Croatia to the northwest, Albania to the southeast, and the Adriatic Sea to the southwest. The capital of Montenegro is Podgorica.

M. Burić
Malo brdo L I/a 13, Podgorica, Montenegro

Z. Nikić (✉)
Faculty of Forestry, University of Belgrade, Kneza Višeslava 1, Belgrade, Serbia
e-mail: zoran.nikic@sfb.bg.ac.rs

P. Papić
Faculty of Mining and Geology, University of Belgrade, Đušina 7, Belgrade, Serbia

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The geological makeup of Montenegro is highly complex. A part of the territory belongs to the Outer Dinarides, and a part to the Inner Dinarides. The geological eras are the Paleozoic, Mesozoic and Cenozoic. Paleozoic formations are largely found in northeastern Montenegro and comprised of Devonian, Carboniferous and Permian rocks. Lithologically, they are represented by sandstones, schists, limestones and conglomerates. Mesozoic (i.e. Triassic, Jurassic and Cretaceous) rocks are widespread in other parts of Montenegro. Triassic formations are represented by flysch, volcanogenic sedimentary and carbonate facies, and volcanic rocks. The carbonate facies is the most extensive. Jurassic and Cretaceous formations are largely represented by limestones, dolomitic limestones, dolomites, marls, sandstones and hornfels. The Cenozoic is comprised of Paleogene, Neogene and Quaternary formations. Paleogene sediments are largely found in the coastal belt and a narrow zone in central Montenegro. Neogene formations are represented by marine and fluvial facies, and Quaternary sediments by alluvial, deluvial, glaciolimnic, glaciofluvial and glacial sediments. The tectonic relationships are highly complex and the result of a turbulent past. In general, most authors identify the following tectonic units in Montenegro: Parahton, Budva–Cukali, Visoki Krš and Mt. Durmitor (Radulović 2012).

The hydrogeological characteristics are governed by the lithological composition and structural porosity of the rocks, spatial positions of permeable and impermeable rocks, and the tectonic assemblage.

Mineral and Thermal Waters of Montenegro

Mineral and thermal waters are found in three hydrogeological zones of Montenegro: coastal, central and Inner Dinarides (Fig. 1).

Coastal Zone (I Zone)

The coastal hydrogeological zone lies along the Montenegrin part of the Adriatic coast. Mineral waters are found in two locations within this zone: one is the southernmost part of the coastal zone (the Ulcinj Riviera area) and the other is the northernmost part of this zone—the Igalo area.

Ulcinj Area (IA)

Thermal mineral water is found in four locations along the Ulcinj Riviera, between the coves of Orašac and Valdanos: Orašac Cove, Ženska Plaža (Women's Beach), Stari Grad (Old City), and Valdanos Cove. Characteristic of all four occurrences is that they are situated at and/or below sea level. Among the four occurrences of

Fig. 1 Hydrogeological zones of Montenegro: coastal, central and Inner Dinarides

thermal mineral water, the most important are those at Ženska Plaža and Valdanos Cove. Ženska Plaža is located in the immediate vicinity of the City of Ulcinj. Valdanos Cove is situated about 5 km (as the crow flies) northwest of Ulcinj.

The extended area of the thermomineral water occurrences in the Ulcinj area is made up of Mesozoic (Cretaceous), Cenozoic (Eocene and Miocene) and Quaternary rocks. In stratigraphic terms, the oldest are Upper Cretaceous/Senonian (K_2^3) rocks found at the highest altitudes north and southwest of the thermomineral water springs. Lithologically, Upper Cretaceous formations are represented by limestones, dolomitic limestones and dolomites. These are hard rocks of cavernous/fractured porosity, well-karstified and generally highly permeable; they represent the main thermomineral aquifer in the Ulcinj area. In relation to the Upper Cretaceous formations, Eocene sediments make up hypsometrically lower parts of the terrain and are represented by flysch. In general, Eocene flysch formations are comprised of two facies: one represented by nummulitic limestones overlying Upper Cretaceous (Senonian) limestones, and the other comprised of marls, sandstones, conglomerates and argillites. Limestone-free Eocene formations are impermeable and constitute a lateral and overlying hydrogeological barrier to the thermomineral water. Miocene sediments are represented by lithothamnion limestones and sandy clays. These sediments discordantly overlie the Upper Cretaceous and Eocene strata. Although they include water-bearing rocks (lithothamnion limestones), the Miocene sediments, as a complex, act as an overlying hydrogeological barrier to thermal waters (Mirković et al. 1978a, b). Quaternary sediments are of no major significance with regard to thermomineral waters in the Ulcinj area.

There are two interpretations of the origin of thermomineral waters in the Ulcinj area. According to Đerković (1986), they are formed and enriched in Miocene sediments. This interpretation is difficult to accept, given relatively high water temperatures, high discharge capacity and, in particular, the nature of water emergence at Valdanos, which cannot be deemed characteristic of Miocene sediments. This is corroborated by the fact that the extent of the Miocene sediments is rather small and their porosity is not sufficient to form permanent springs of the high capacity as already assessed. According to Perić (1982) and Burić (1985), the water is formed and enriched in the deep reaches made up of Cretaceous sediments, in contact with anhydrite and sea water. The Miocene sediments are only a transit zone for the thermomineral water toward the ground surface and actually an impermeable roof.

The composition of these thermomineral waters can be attributed to the deep reaches of the terrain and the effects of anhydrite and gypsum, as well as hydrogen sulfide coming from still deeper reaches, through fault zones. The high discharge capacities, such as those of the Valdanos Cove springs, certainly cannot trace to Miocene sediments. Additionally, the mineral water occurrences at Valdanos Cove originate in Upper Cretaceous limestones, along their interface with Eocene flysch. On the basis of chemical results mineral water is of Na–Cl type with TDS up to 31 g/L and temperature up to 24 °C. The secondary characteristic of the chemical composition are sulphates, calcium, magnesium and hydrogen sulfide (Table 1; Fig. 2).

The thermomineral waters at Ženska Plaža diffuse below sea level, largely through recent strata that cover the sea floor made up of Miocene sediments in that area. In places, they also emerge from sea sand and gravel, visible at times of low tide or waves. Sulfur flakes and white film on the sea floor mark the points of emergence. Streamlines can be discerned in places with sulfur flakes, but nowhere has hydrostatic pressure been able to surmount the upper layer of sea water and, therefore, the emergence of thermomineral water is not apparent on the surface of the sea. However, the level of emergence of thermomineral water has changed over time. In the past, the springs at Ženska Plaža used to discharge water above the

Table 1 Chemical composition of mineral and thermal waters in Montenegro

	Ulcinj Ženska plaža	Igalo	Ilidža Komarnica	Đuranovića Luka	Čeoče	Nedakusi	"Rada" (label)	Bogajski potok
T, °C	24	15	26.3	5–13	12	11	–	–
pH	7.7	8	8	5	6.25	6.35	–	6.4
TDS, mg/L	31,000	4600	245	45	1570	2320	1395	17,000
Ca, mg/L	1122	110	62	6	210	205	210	15
Mg, mg/L	1026	122	12	4.8	48	70	49	143
Na, mg/L	9324	1460	4	2	300	680	329	4508
HCO_3, mg/L	122	232	152	60	1232	2270	1220	8845
SO_4, mg/L	660	100	60	11	323	400	212	2
Cl, mg/L	18,800	2590	11	10	59	96	51	2485
CO_2, mg/L	10	–	–	1760	700	2500	5000	950
$KMnO_4$, mg/L	15.5	30	2	0.8	–	–	–	80
Water type	Na–Cl	Na–Cl	Ca–HCO_3	Mg, Ca–HCO_3	Na, Ca–HCO_3	Na, Ca–HCO_3	Na, Ca–HCO_3	Na–HCO_3, Cl

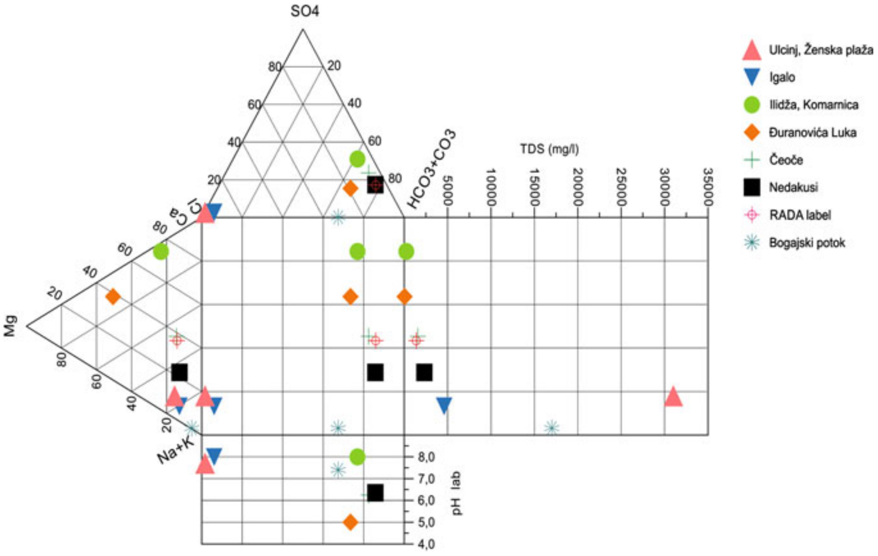

Fig. 2 Durov diagram of mineral waters in Montenegro

coastline, such that the water was captured and used. Even today there are remnants of an old spring cap. The level of emergence decreased continuously and after the 1979 earthquake it was lowered to or below sea level.

In view of the way thermomineral waters emerge in the Ulcinj area, no direct hydrological surveys can be made. It has only been possible to assess the capacity of the thermal springs. It is safe to assume that more than 10 L/s of mineral water of 24 ° C can be withdrawn at Ženska Plaža by a suitable method. Bacteriological analyses of the thermomineral water at Ženska Plaža have indicated that the water was sterile. In view of its type and origin, this water appears to be protected from pollution.

According to the balneological classification of thermomineral water, the water at Ženska Plaža is warm, radioactive, sulfurous mineral water of the sodium–chloride type. The radium concentration of this water is rather high, 39.1 Bq/L. Based on its composition, especially the hydrogen sulfide concentration and radioactivity, the thermomineral water at Ženska Plaža us suitable for a health spa, for bathing in tubs or pools. In combination with peloids, which are abundant in the Ulcinj area, the water can be used for medicinal purposes—the same as the peloids. This relates to both heat and the chemical effect. At Ulcinj, the water can be used to help treat disorders of the locomotor system (chronic rheumatic and other bone, joint and soft tissue ailments), chronic inflammatory gynecological conditions and some skin disorders. The medicinal properties of sulfurous mineral waters are well known; given the spring discharge capacity and temperature of the water at Ulcinj, it can be a contributor to the tourist offering and development of health tourism.

Igalo Area (IB)

Igalo is the only developed seafront spa town in Montenegro. It is located in Sutorina, where the Sutorina River empties into Topla Cove of the Bay of Kotor. It is only 2.5 km away from the City of Herceg Novi. The Igalo health spa was established in 1949 (Marković 1980). Mineral water springs in Igalo occur along a roughly straight line, NW–SE, between Prevlaka to the east and Sutorina to the west, including the Njivice area. The largest spring was captured back in 1960 and is used for treatment purposes by Dr. Simo Milošević Health and Rehabilitation Institute in Igalo.

The geology and tectonic relationships of the lithological members at Igalo and its immediate surroundings are highly complex. Looking from the coastline (south) toward Mt. Orjen (north), there are alternating anticlinal and synclinal structures comprised of Upper Cretaceous (Senonian, K_2^3) carbonate rocks, Middle Eocene (E_2) limestones, and Upper Eocene (E_3) flysch. The Upper Cretaceous, Senonian and carbonate complex is lithologically represented by limestones and dolomites. These carbonate rocks make up the immediate hinterland (Košara and Vitalina) and likely also the watershed and mineral water aquifer. The carbonate rocks are massive and banked, tectonically broken up and karstified. They are highly permeable and constitute the main mineral water bearing medium of Igalo (Burić 1993). There are numerous occurrences of bauxite between the limestones and Middle Eocene nummulitic limestones. The Middle Eocene nummulitic limestones are stratified and banked, and they transgress Senonian limestones. The strata dip at an angle of 60°–70° to the northeast (toward Igalo). Upper Eocene flysch sediments make up the bottom of the Sutorina Valley. The Upper Eocene flysch is comprised of marls, argillites and conglomerates (Antonijević et al. 1973). The layers are rather folded. Quaternary formations overlie the Upper Eocene flysch in the Sutorina Valley. They are made up of sand and gravel sediments, which are about 20 m thick at the mouth of the Sutorina (Burić 1993).

In tectonic terms, the relationships between the Upper Cretaceous and Middle Eocene limestones to the Upper Eocene flysch, and a deep fault trending NW–SE, near Sutorinsko Polje, are the most important elements. Mineral waters emerge along this fault, between Njivice and Igalo. The tectonic contact between the carbonates and the Upper Eocene flysch is very steep, as is the dip of the fault itself and the carbonate layers (up to 70° to the northeast). There are also numerous local faults. With regard to the formation of mineral waters in the area, Upper Cretaceous and Middle Eocene carbonate rocks are especially important as, according to Đerković (1985), mineral waters in the upper reaches are mixed with water infiltrated from the surface of the surrounding limestone terrain.

The origin of mineral waters in the Igalo area has not yet been reliably established. Based on the results of surveys conducted to date, it is reasonable to assume that the Upper Eocene flysch sediments are impermeable and that they constitute a hydrogeological barrier, while the Upper Cretaceous and Middle Eocene limestones are permeable rocks holding a karst fractured aquifer, where the limestones are the main conveyors of mineral water in the area. The mineral waters that emerge at several springs between Njivice and Igalo are considered to be vadose waters infiltrated from the ground surface through pores and fractures, which gravitationally, along tectonic discontinuities and karst conduits, reach deeper strata through Mesozoic and Paleogene carbonate rocks. The infiltrated waters become enriched with minerals in the carbonate rocks, and are then driven to the ground surface by hydrostatic pressure. They emerge along the lowest base level of erosion and the contact between the impermeable Upper Eocene flysch and Middle Eocene carbonate rocks, which are in direct contact with Senonian carbonate rocks. In shallower parts, deep groundwaters mix with surface water infiltrated between Košare and Vitalina (in the hinterland) and sea water, acquiring their ultimate chemical composition. This interpretation is acceptable when the waters of Igalo are viewed as mineral waters, which they are, compared to ordinary groundwater. Still, their chemical composition indicates that they could also be similar to ordinary groundwater from limestone terrains, which is mixed with nearby sea water (Burić 1993).

On the basis of chemical analysis mineral water is of Na–Cl type, with TDS up to 4.6 g/L and the temperature up to 15 °C. The secondary characteristics of chemical composition are sulphates, calcium and magnesium, and elevated contents of organic matter.

All mineral water springs at Igalo discharge along the previously-mentioned fault, in the form of several jets at the point of emergence on the ground surface. However, the primary points of discharge are covered by recent sediments created after pieces of rock became dislodged and fell down a steep slope. The springs are situated at the foot of that slope. The fact that the primary points of emergence of significant amounts of water are covered by considerable rock material is one of the reasons that precluded proper discharge surveys. It is realistic to assume that mineral waters emerge from fractures, near the coastline, and a little higher in some places (Burić 1993). Only occasionally made estimates of spring discharges at Igalo are available. Data of the highest reliability were collected as part of a hydrogeological survey conducted in 1984. According to that survey, the discharge of the largest captured spring was from 6 L/s in the summer to more than 30 L/s in May 1984, at which time an estimated 8 L/s of additional water emerged untapped below the capture. The discharge of the smaller spring was estimated at 6 L/s, and that of the second largest at 10 L/s (Đerković 1985).

When considering the use of Igalo's mineral waters, it should be kept in mind that they have been classified as such based on the mineral content criterion. This also applies to the quality of the cold mineral waters in Igalo and their suitability for use. In this regard, the balneological significance of the largest spring used for health and rehabilitation purposes by Dr. Simo Milošević Institute has been identified. The mineral water is used for drinking in the case of stomach, intestinal and gall bladder ailments and anemic and lymphatic conditions. At Blatija, mineral water is mixed with medicinal mud, as well as used for post-treatment showering and bathing in tubs. Heated water is used to treat rheumatic muscle and joint ailments, neuralgia and female reproductive organs (Marković 1980). There is a source of sea mud, of mineral-and-plant origin, adjacent to Igalo's seafront. It is used in fangotherapy. The mud is diluted with water to a certain density and heated up to 50 °C (the temperature is adjusted to the patient's needs).

Central Zone, Komarnica Canyon (II Zone)

The only spring in Montenegro that discharged water with a temperature above 25 °C was Ilidža Spring in the canyon of the Komarnica River, a right tributary of the Piva, which belongs to the Drina River Basin (and consequently to the Black Sea Basin). Because of the high temperature, Ilidža Spring was designated a natural rarity of Montenegro. Past tense is used here because Ilidža Spring was flooded after the 220 m high arch concrete dam "Mratinje" was built on the Piva River in 1976, and the Piva Reservoir created. The water level of the Piva Reservoir is always above the spring, so it is not possible to undertake any measurements or conduct surveys. Given the fact that Ilidža Spring was the only natural occurrence of high-temperature water in Montenegro, provided below are the results of surveys conducted before impoundment of the Piva River.

Ilidža Spring is located at the bottom of the canyon of the Komarnica River, some 5.5 km upstream from the mouth of the Komarnica, which empties into the Piva. It is situated at an altitude of 610 m, below the flood stages of the Komarnica. After Mratinje Dam was built and the Piva River impounded, the spring was submerged to some 60 m below the maximum water level of the Piva Reservoir.

Prior to flooding, water emerged at Ilidža Spring through alluvial sediments of the Komarnica River, comprised of sandy gravels. Adjacent to the then alluvial plain of recent origin, there are conglomerates that represent the old river terrace of the Komarnica. These rocks overlie Middle Triassic/Ladinian stage (T_2^2) dolomitic limestones, in which the river channel is incised and which make up the sides of the Komarnica Valley. Relatively close to the spring there are Middle Triassic (T_2) igneous rocks, which have broken through limestones on the ground surface or are, probably, just below the ground surface. These Middle Triassic igneous rocks are lithologically represented by andesites, dacites, rhyolites, trachytes and keratophyres (Mirković 1980). They are found along faults and within the riverbed, and are exposed on the ground surface to a greater or lesser extent. The Middle Triassic carbonate rocks are underlain by Lower Triassic formations (T_1), lithologically represented by marls, limestones and sandstones. According to Burić (1985), the main thermal aquifer, Ilidža, is a Mesozoic carbonate complex, which contains Triassic eruptives. The immediate terrain around the spring has also been flooded by the Piva Reservoir. Groundwater is of Ca–HCO3 type with low TDS up to 250 mg/L. It is the thermal water with temperature up to 26 °C.

The point at which Ilidža Spring discharged water on the ground surface was secondary. The primary point was covered/masked by alluvial sediments (sandy gravels) of the Komarnica River, and was an open fracture in Middle Triassic limestones. The spring was of the ascending type. Based on available information, it is reasonable to assume that atmospheric precipitation and surface water infiltrated from the ground surface around Mt. Durmitor reached the Lower Triassic and Middle Triassic sedimentary rocks and Triassic eruptives. The water became heated and enriched in the deeper reaches. Then, under hydrostatic pressure, the thermal water was discharged along the empty fracture system of a fault in the Komarnica Valley, in the zone of the lowest base level of erosion (the channel of the Komarnica).

During the summer (or the low-flow period), thermal water emerged from a shallow depression in the alluvial sediments, lithologically represented by sandy gravels. The discharge rate did not exceed 0.1 L/s. Given that this was the secondary point of discharge of thermal water of Ilidža Spring, which reached the ground surface almost vertically through the alluvium, it is reasonable to assume that the primary discharge rate was much higher. The secondary thermal water dispersed through alluvial sediments (estimated depth 0.8 m), resulting in the above-mentioned discharge rate (Burić 1985).

Inner Dinarides Zone, Lim and Ibar Catchments (III Zone)

More than 30 occurrences of mineral water have been registered in northeastern Montenegro which, in geotectonic terms, belongs to the Inner Dinarides. Most of these occurrences are well known, since ancient times. The springs generally discharge cold mineral water, mostly characteristic for their carbon dioxide content. The spring discharge, of the diffuse type, is low in the natural regime (less than

0.1 L/s), with the exception of Čeoče Spring at Bijelo Polje. All the springs in northeastern Montenegro, which deliver cold carbonated mineral water, are associated with the Paleozoic flysch complex and the eruptives within this complex that are probably Triassic. Characteristic of the Paleozoic flysch complex, in tectonic terms, is that the rocks are extremely broken up and, intersected by many fractures and fissures, along which mineral water spews (Milojević 1955). With regard to the utilization potential, the carbonated mineral waters in this area are among the most prospective in Montenegro. It is likely that the hydrogeological structures within the Paleozoic formations include a large geothermal anomaly, which is conducive to the generation of CO_2 in the extended area (Protić and Andjelković 1999).

Based on the density of the occurrences of cold mineral waters in northeastern Montenegro, two distinct areas are identifiable. One is near Rožaje, in the catchment area of the Ibar River, and the other near Bijelo Polje, in the catchment area of the Lim River. Most of the cold carbonated mineral water springs in the Rožaje area are found in the valley of the Županica River. Additionally, in the Rožaje area, but not within the Županica catchment, there are two more occurrences of cold carbonated mineral water: Bašča and Lučice, whose discharge is less than 0.1 L/s. Among the above-mentioned springs, detailed hydrogeological research in the Rožaje area has been conducted only in the Županica Valley (i.e. at Đuranovića Luka and Bogajski Potok), such that they are better known than the others. Most of the mineral springs in the Bijelo Polje area are found in the valley of the Lješnica River (a right tributary of the Lim), where in addition to some 15 low-capacity springs there is the largest Čeoče Spring. This area also hosts cold carbonated mineral water springs, one each at Andrijevica (Kralje) and Plav (the Trokutska River). Apart from Čeoče Spring, whose water is commercially bottled, the other spring in the area that deliver natural carbonated mineral water are of a very low capacity and suitable for use only under natural conditions.

Mineral Water Springs Near the Town of Rožaje, Catchment Area of the Ibar River

Đuranovića Luka Spring

Đuranovića Luka Spring is located about 8 km west of Rožaje. The spring itself is at an altitude of 1170 m, in the valley of a creek that is a left tributary of the Županica River. Even though its discharge capacity is low, this spring was registered back in the 1930s and initially named “Rožaje Carbonated Springs”, mentioned by Ščerbakov (1922). Its attraction is largely a result of the chemical composition of the water, with relatively high concentrations of CO_2, SiO_2 and Fe, and a low pH level. Special-purpose surveys of this spring were conducted in the 1970s and 80s.

Đuranovića Luka Spring emerges from clay debris, up to 3 m thick, which covers a significant area where ordinary and mineral waters are discharged. Mineral waters trace to black Devonian/Carboniferous (D, C) schists and schistose sandstones. These Paleozoic formations are lithologically represented by sandstones, conglomerates, phyllite-argillic schists and limestones (Mojsilović and Bakalić 1984). In their immediate vicinity there are Lower Triassic (T_1) sedimentary rocks (conglomerates, sandstones, breccias and argillites) and Middle Triassic (T_2) eruptives (porphyries, quartz keratophyres, tuffs). In the mid 1970s, a 150 m deep exploration well was drilled near Đuranovića Luka Spring and used to identify the Upper Carboniferous (C_3) lithological complex, which is represented by quartz-sericite schists, comprised of calcite, silica and, to a lesser extent, mica. Apart from organic matter, these rocks contain graphitic substances and metallic minerals. The schists alternate with sandstones. In places, the biomicrosparites in this series trace solely to flora remnants. However, the tectonic and geological relationships in the area have not been sufficiently clarified. It has generally been established that the Đuranovića Luka Spring area belongs to the core of an anticline made up of Paleozoic schists and sandstones. There are many fractures in the schists, along which the mineral water emerges. The fractures are connected to a deep fault, running along the Županica, which provides a pathway for the carbon dioxide gas from the deeper reaches to the ground surface.

The natural point of emergence of Đuranovića Luka Spring, where the water diffuses to the surface through clay debris, was found to be its secondary outlet. After about half a meter, the water sank back into the clay debris. An exploratory cut removed the clay debris and uncovered the primary point of emergence, comprised of fractures in Paleozoic schistose sandstones. In terms of the natural discharge pattern, this spring features a combined mechanism, where the cause of emergence is largely the action of gas flow with water, and partly due to local pressures in the case of jets. The spring is of the ascending type. However, the hydrogeological conditions in which the water is formed have not yet been determined. A part of the water emerges along the fault, through Paleozoic schists, probably from a depth of more than 1000 m, and the remainder from parts closer to the ground surface.

Analyses of Đuranovića Luka Spring's water quality indicate that the water temperature ranges from 5.2 to 13 °C, that the water is of the magnesium, calcium–hydrocarbonate type of carbonated, iron-enriched cold mineral water, containing more than 2 g/L of CO_2 and 10 mg/L of iron. TDS is of less than 100 mg/L. Balneological testing of the water has shown that it can be used as mineral water for drinking, to support treatment of certain chronic ailments (chronic hypoacid gastritis and urinary tract sand). The water is currently not used for medicinal purposes in an organized manner, only by the local population as needed.

Bogajski Potok Spring

Bogajski Potok Spring is located near the mouth of the Bogaj Creek, which empties into the Županica River. The results of investigations indicated that TDS was elevated (greater than 1 g/L); the concentrations of hydrocarbonates, and especially of chlorides and sodium, were found to be high. An exploration well was drilled to a depth of 410 m in the mid-1980s.

The geology of the area, the type and origin of the water and the discharge capacity of Bogajski Potok Spring are nearly identical to those of the previously described Đuranovića Luka Spring, and will therefore not be repeated. It should be emphasized, however, that the discharge rate is less than 0.1 L/s. Based on chemical composition mineral water is of Na, Ca–HCO_3, Cl-type CO_2-rich mineral water with TDS about 17 g/L, and CO_2 content up to 1 g/L.

Mineral Springs Near the Town of Bijelo Polje in the Catchment Area of the Lim River

Čeoče Spring

In northeastern Montenegro, in the extended area of the town of Bijelo Polje, there are numerous occurrences of mineral water along the slopes of Mt. Lisa (alt. 1509 m). Montenegro's cold carbonated mineral water spring of the highest capacity is located about 5 km northwest of Bijelo Polje, within the valley of the Lješnica River, a right-hand tributary of the Lim River. Under natural conditions, the spring was situated about 20 m above the river channel, at a distance of some 30 m. Its altitude is roughly 550 m. It has been known as Čeoče Spring since ancient times.

In the extended area of Čeoče Spring the oldest rock formations are Devonian (D). They are lithologically represented by sandstones, conglomerates, phyllite argilloschists and limestones. In general, the formations hold no aquifers, apart from carbonate lenses with local water-bearing layers of low capacity. The Devonian formations are overlain by a thick complex of Carboniferous/Permian (C, P) metamorphic rocks. They are lithologically represented by sandstones, schists and crystalline limestones (Živaljević et al. 1984). The schists are yellow, greenish and purple, heavily wrinkled and chipped. From a hydrogeological perspective, the rock complex is characterized as largely impermeable, with rare local permeable zones along major fractures and fault zones. There is a fault running along the channel of the Lješnica River, where Čeoče Spring is situated. Its trending is NW–SE. The Carboniferous/Permian schists contain lenses of limestones, marble and white quartz. These carbonate formations include a large-volume karst-fractured aquifer. Čeoče Spring is genetically associated with this type of aquifer, or thick carbonate lenses. The Carboniferous/Permian formations, with minor breakthroughs, are lithologically represented by quartz–diorites and quartz–keratophyres. These eruptive veins are not extensive on the ground surface but are intersected by numerous fractures and fissures, such that they crush easily. The youngest rock formations are Quaternary, represented by fluvioglacial sediments. They are clastic, of intergranular porosity, and unconsolidated to poorly consolidated. Downstream from the spring there is a small mass of deposited calc tufa, as a result of sedimentation of $CaCO_3$ from the spring water at Čeoče. It should be noted that only this spring deposits calcium carbonate in the form of calc tufa.

A survey undertaken in 1982 indicated that a useful mineral water aquifer is situated at a depth of up to 26 m (Burić 1993). It is represented by Paleozoic, fractured, thin-layered quartzite–sericite marbles. From there, under hydrostatic pressure, the water travels to metamorphic rocks but also upper reaches of alluvial sediments. However, the main zone in which mineral water discharged by Čeoče Spring is formed is the deep zone of Paleozoic metamorphic rocks, particularly marbles. Carbon dioxide plays a primary geochemical role in the formation of these mineral waters. It likely traces to thermometamorphic processes, which take place in the deeper strata (Protić and Andjelković 1999). Given the primary role of CO_2, these waters can also be formed at smaller depths, of the order of several tens of meters. Water-rock interaction is an important driver of the mineral content of water and since the conditions for slow water exchange are favorable in metamorphites, there are numerous mineral springs in the vicinity of Bijelo Polje. The natural yield of Čeoče Spring is also a result of the size of porosity of the fractured and karstified marbles. On the other hand, the formation of carbonated mineral waters in this area is also probably related to the presence of a geothermal anomaly, which is most likely caused by a large igneous intrusive (Protić and Andjelković 1999). It is possible that a zone of relatively porous metamorphites exists around the intrusive, such that in this hydrogeological setting it is a potential mineral water aquifer (and warm mineral water might be abstractable in this zone). According to Protić and Andjelković (1999), such an intrusive is also indicated by calc tufa deposits in the immediate vicinity of Čeoče Spring, which suggests that the present cold mineral water spring discharged warm mineral water in the recent past which, as the intrusive gradually cooled, became cooler at the spring. In general, Čeoče Spring is of the ascending type and its water is genetically associated with a fractured aquifer within marble lenses of the Paleozoic schists.

According to the mineral water discharge surveys at Čeoče Spring in 1971, the discharge ranged from 1.80 to 0.75 L/s, and the average was Qav = 1.22 L/s. However, for the purposes of the bottling plant, the minimum spring discharge of 0.75 L/s was taken as the design discharge. This is the only carbonated water spring in Montenegro whose discharge under natural conditions is greater than 0.1 L/s. Mineral water is of Na, Ca–HCO_3 type, CO_2-rich mineral water with TDS up to 1.6 g/L, and CO_2 content up to 1 g/L (bottled water “Rada”).

Nedakusi-Šljepašnici Springs

Nedakusi Springs are located about 4 km northeast of Bijelo Polje. The spring is at an altitude of about 500 m. There are three small mineral water springs in this valley: Nedakusi Gornji (Upper Nedakusi), Nedakusi Donji (Lower Nedakusi) and Šljapešnica.

The extended zone of Nedakusi Springs, and the points of emergence, are made up of Paleozoic Permian–Carboniferous formations. They are lithologically represented by schists and sandstones, which include limestone lenses and irregular white quartz lenses (Živaljević et al. 1984). The spring site is comprised of tectonically extremely broken up phyllites and argilloschists. Along the left-hand side of the ephemeral stream the strata are at an angle of 20°, dipping to the southeast, and on the right-hand side they dip 30° to the northeast. This discordance is largely the result of a fault trending NW–SE along the stream, which is for the most part covered by river sediments. In addition to the main fault, which has caused different positions of most of the terrain, there are smaller faults and fractures which give the rocks a crushed and generally broken-up appearance. As a result, these rocks weather easily into debris that covers the parent rocks. Rock degradation near the fault has also been aided considerably by groundwater flow along the fault (Milojević 1955).

All three springs (Nedakusi Gornji, Nedakusi Donji and Šljapešnioca) are of the ascending type. They emerge on the ground surface in places where the water has penetrated debris, which overlies a fracture in Paleozoic schists. The water is genetically associated with fractures and tectonic discontinuities in the deeper reaches of the Paleozoic schists (Milojević 1955). Based on chemical composition groundwater is of Na, Ca–HCO_3 type CO_2-rich mineral water with TDS up to 2.3 g/L, and CO_2 content up to 2.5 g/L. All three springs are used occasionally only by the local population. At Nedokusi Gornji Spring, the water emerges accompanied by a small amount of CO_2 gas.

Other Cold Carbonated Mineral Water Springs Near Bijelo Polje in the Catchment Area of the Lim River

In addition to the largest-capacity Čeoče Spring, there are numerous other cold carbonated mineral water springs in northeastern Montenegro—in the catchment area of the Lim River. In general, mineral water occurrences near Bijelo Polje are found in an area of 150 km^2, which corresponds to the size of the hydrogeological structure in which carbonated mineral water is formed (Protić and Andjelković 1999). The water discharged of all these springs is periodically accompanied by small amounts of gas, associated with terrains whose basic geology is made up of Paleozoic schists and to the other previously-mentioned lithological members. In view of their low capacity, these springs were not deemed prospective for commercializing and, as a result, remain hydrogeologically under-explored. Still, from a hydrogeological perspective, as well as from that of the local community, they represent an attraction that could provide certain opportunities.

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Mineral and Thermal Waters of Serbia: Multivariate Statistical Approach to Hydrochemical Characterization

Maja Todorović, Jana Štrbački, Marina Ćuk, Jakov Andrijašević, Jovana Šišović and Petar Papić

Abstract A new approach using hydrochemical characterization of mineral water in Serbia was applied in this paper. After field research and groundwater sampling, laboratory measurements were conducted. Trace and ultratrace elements in 174 samples of mineral water were analyzed using HR ICP–MS and methods to determine gross alpha/beta activities were applied. Hierarchical cluster analysis (HCA) was used on selected variables: major ions (Ca, Mg, Na, Cl, HCO_3, SO_4), Si, temperature, electrical conductivity (EC), pH and Eh. Results showed that variability of chemical characteristics, and diverse mineral and thermal water types were grouped into six clusters. Geochemical conditions of each cluster were considered in detail in terms of basic hydrochemical parameters, geological characteristics, and the contents of particular elements. There were certain regularities among the separated groups. Water differed in temperatures, dissolved mineral substances, pH, Eh values and gas content, which indicated different hydrogeological conditions. Variations among clusters in natural radioactivity, the content of essential elements and rare earth elements (REE) are also discussed.

Keywords Mineral water · Thermal water · Hydrogeochemistry · HCA · Serbia

Introduction

Mineral and thermal waters are a special kind of groundwater, distinguished by specific chemical or physical properties such as higher mineralization, concentration of certain constituents, dissolved gas, radioactivity, or temperature. Mineral or thermal waters are usually connected with specific and unique geological and tectonic structure (Laboutka and Vylita 1983).

M. Todorović (✉) · J. Štrbački · M. Ćuk · J. Andrijašević · J. Šišović · P. Papić
Faculty of Mining and Geology, University of Belgrade, Đušina 7, 11000 Belgrade, Serbia
e-mail: maja.todorovic@rgf.bg.ac.rs

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Chemical elements that make up the groundwater composition can be divided into several groups, macrocomponents (major components), trace elements (element concentrations in water usually less than 1 mg/L) and ultratrace elements (concentrations below 0.1 mg/L) (Matthews 1982; Dimitrijević 1988; Filipović and Dimitrijević 1991). The recent development of high–sensitivity equipment, namely Inductively-Coupled Plasma Mass Spectrometers or ICP–MS, has contributed to the detection of trace and ultratrace elements in water. Thus, until recently, elements such as rare earth elements, were not detected in groundwater.

Analysis of the macro and micro components of groundwaters has proven to be very important from theoretical and practical aspects. Some elements are established as being essential for human health (Ca, P, Mg, F, Na, K, Cl, Zn, Cu, Se, Mg, Mn, Mo, Fe, I, Cr) (WHO 2011). The concentration of each element in groundwater is to a greater or lesser degree dependent on the concentrations and speciation of the other elements in solution and on parameters such as pH, Eh and temperature.

Numerous mineral and thermal water springs are located on Serbian territory, where 230 mineral and thermal springs have been thoroughly studied (Filipović 2003). With regard to geothermal resources in Serbia, of particular importance are those in the Pannonian basin and its circumference (hydrogeothermal system of Mačva), as well as the central and southeastern part of Serbia. On a global geothermal map, Serbia is indicated as a country in which the thermal and mineral waters are used mainly for balneological purposes, recreation and bottling. They are also used in agriculture, aquaculture, industry and technology. Exploitation of thermal and mineral waters in Serbia has a much longer history than scientific research. Hot spring baths, for bathing and rehabilitation, have been used since Roman times (Joksimović and Pavlović 2014).

This study covered a wide range of major, trace and ultratrace elements, and also investigated the natural radioactivity of mineral and thermal waters. The goal of the research was to present new data of 174 occurrences of mineral and thermal waters from Serbia and to classify waters in groups according to their chemical similarities using multivariate methods.

Methods

Field and Laboratory Measurements

Groundwater samples of 174 mineral and thermal waters from wells and natural springs were collected in 2012–2014 (Fig. 1). The oxidation/reduction potential (Eh), pH values, electrical conductivity and water temperatures of samples were determined in-situ using a portable Field Case (WTW pH 3110 SET 2 and Electrode Sen Tix ORP 100 °C).

Major cations (Ca, K, Mg and Na) in the groundwater samples were measured by inductively-coupled plasma optical emission spectrometry (ICP–OES). Major anions were determined by ion chromatography (Dionex ICS–3000 DC). Trace

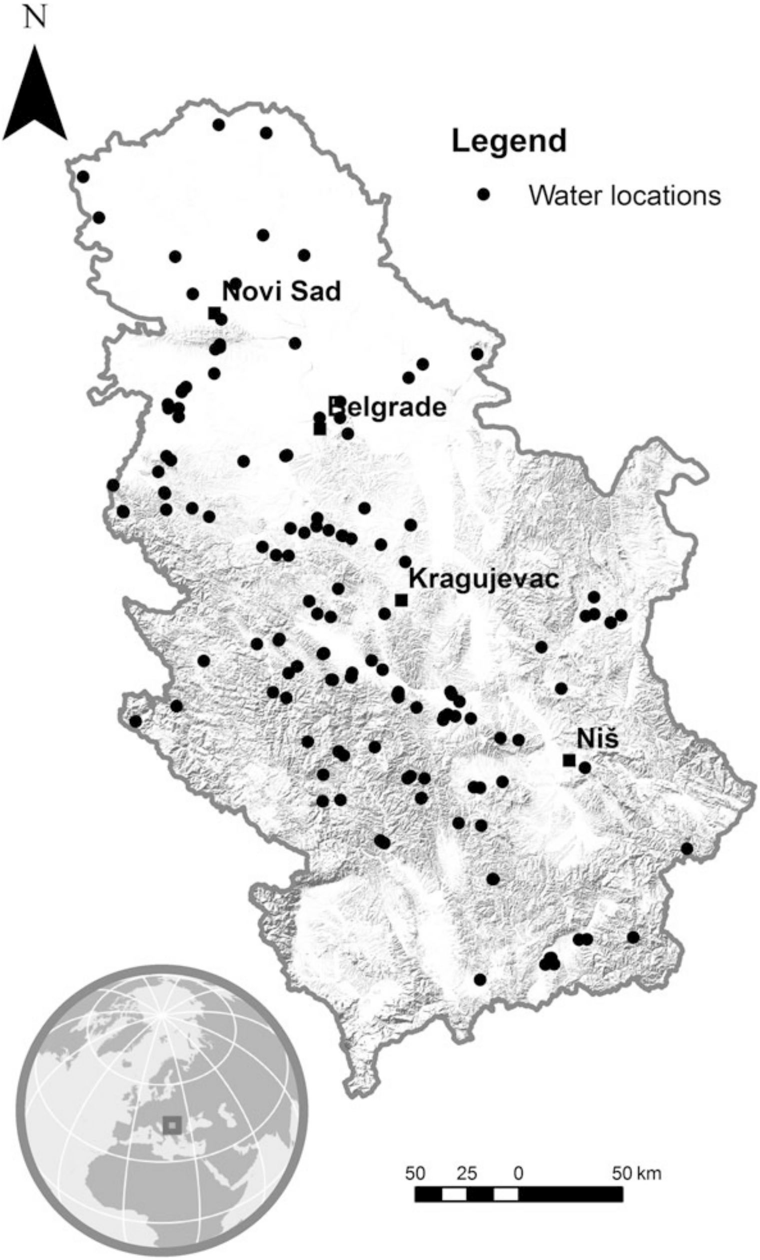

Fig. 1 Study area and locations of groundwater samples

element concentrations in the groundwater samples were measured using high resolution inductively-coupled plasma mass spectrometry (HR ICP–MS).

The method to determine gross alpha/beta activities was based on the evaporation of 3 L of the water sample under UV lamps and calcining at 550 °C to a constant mass. Suitable-geometry measurements were made on a low level proportional counter Thermo–Eberline FHT 770T, featuring a 21 % efficiency for alpha radiation and 33 % for beta radiation. The sample measurement time was 3600 s. For determining gamma-emitter radionuclide activity, 8–10 L of water sample was evaporated to a volume of 200 mL and transferred to polyethylene vessels. The sample was measured on a gamma spectrometer with a HP Ge detector, whose relative efficiency was 23 %. The detector was calibrated using standard radioactive reference material, MIX–OMH–F. The duration of sample measurements was 1.3 days, depending on the concentrations present.

Statistical Analysis

Each sampling site was characterized by a large number of chemical and physical variables, making the regional hydrogeochemical study a multivariate analysis. Multivariate statistical analysis is a quantitative approach to groundwater classification allowing the grouping of groundwater samples and making correlations between chemical parameters and groundwater samples. In this study, hierarchical cluster analysis (HCA) was applied using Statistica version 6.1. Cluster analysis is a multivariate method which aims to classify a set of observations, e.g. groundwater samples, on the basis of the extent of similarity of their physical and chemical characteristics, into a number of different groups (clusters). Members of the resulting groups are similar to each other but distinct from members of other groups. In this case, each group would represent a different hydrochemical type of mineral water, regarding differences in their physical and chemical characteristics.

This hierarchical clustering was developed using a combination of the Ward's linkage method (Ward 1963) and squared Euclidean distance (Massart and Kaufman 1983), as a measure of similarity between samples. It was concluded that the combination of these two techniques would give the most diverse clusters, which is the aim of the HCA. The result of this statistical method is a graphical representation of extracted groups—dendrogram (Güler et al. 2002; Wanda et al. 2011). The classification of samples into clusters is made on the basis of visual inspection of the dendrogram (Cloutier et al. 2008), which implies a degree of subjectivity of the results (Güler et al. 2002). All samples whose squared Euclidean distance is less than the *phenon line*, fall into one cluster (Sneath and Sokal 1973). The phenon line is chosen so that differences in the hydrochemical characteristics of extracted clusters are pronounced (Oyebog et al. 2012).

Data screening of the 174 mineral water samples showed the necessity for removal of 14 samples, because of an electroneutrality greater than 5 % or incomplete chemical analyses. Thus, a total of 160 mineral water samples was included in further statistical analysis. Major ions: Ca, Mg, Na, Cl, HCO_3, SO_4 and Si, as well as temperature, electrical conductivity (EC), pH and Eh were used in the cluster analysis. Before conducting HCA, data normalisation was carried out as necessary. Selected parameters were subjected to Box-Cox transformation (Box and Cox 1964), and data for 11 variables were standardized by calculating their standard scores (z-scores). Standardization scales the Box–Cox transformed data to arange of approximately −3 to +3 standard deviations, centered about a mean of zero. In this way, each variablehas equal weight in the statistical analyses (Güler et al. 2002).

Cluster analysis was applied on Box–Cox transformed and standardized data to determine whether it would be possible to classify the selected 160 mineral water samples into hydrochemical groups or facies that would be meaningful, not just in a statistical, but also a geological context.

Geochemist's Workbench (GWB) software was used for establishing the water types and hydrochemical diagrams.

Results and Discussion

General Characterisation of Mineral and Thermal Waters of Serbia

Results show a large variability of chemical characteristics and diverse water types. Temperatures ranged between 8 and 106 °C, Eh from −226 to 426.5 mV, EC between 95 and 28 925 μS/cm. Regarding pH values, waters were slightly acidic to alkaline (5.75–9.72). The predominant facies of these waters could be grouped into three large families: hydrocarbonates (95 % of mineral waters), chlorides (3.75 %) and sulphates (1.25 %).

Hierarchical Cluster Analysis

A regional hydrogeochemical study is a multivariate problem because of a large number of chemical parameters (variables) associated with a large number of sampling sites (observations). Although multivariate statistical methods do not indicate cause-and-effect relationships, they provide information from which such relationships can be inferred (Monjerezi et al. 2011). Therefore, hierarchial cluster analysis was used to classify groundwaters and to discover major mechanisms influencing groundwater chemistry.

The results of hierarchical cluster analysis of the 160 samples are shown in the dendrogram (Fig. 2a). The classification of groundwater samples was based on visual inspection of the dendrogram. Greater or fewer groups could be defined by

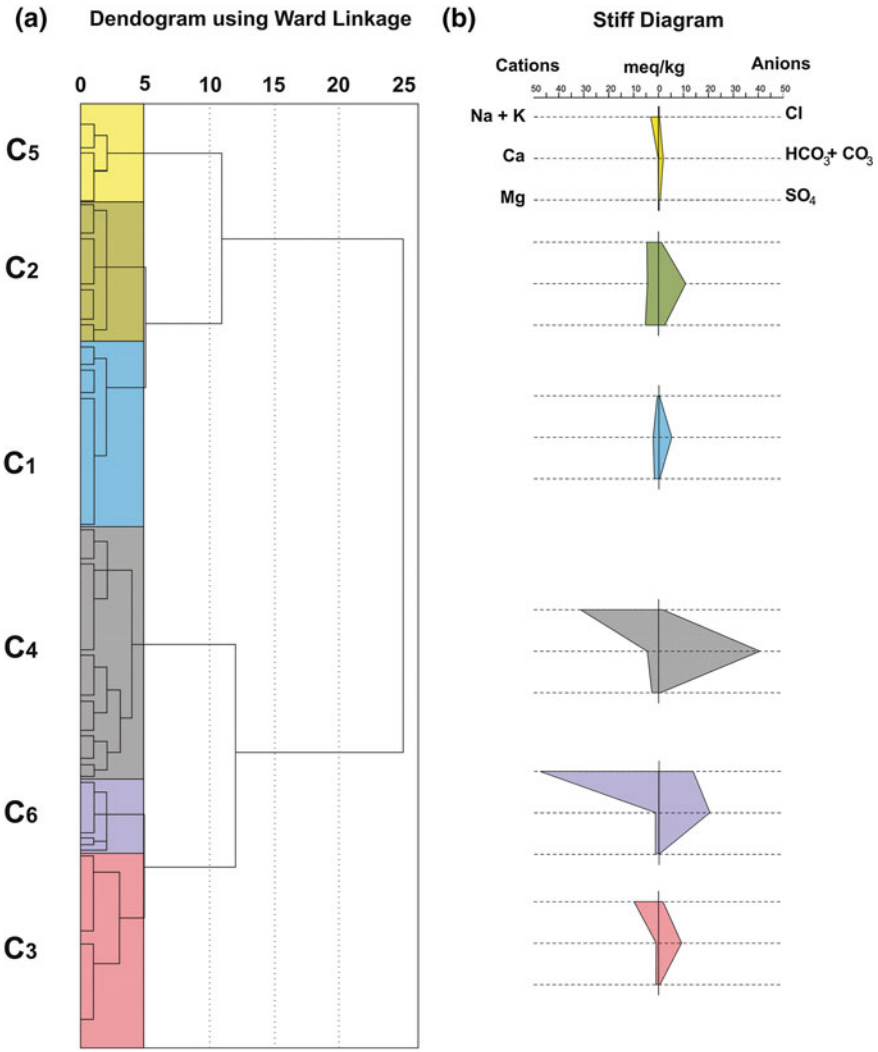

Fig. 2 **a** The dendrogram showing the six clusters. **b** The stiff diagrams showing the average compositions of each cluster

moving the Phenon line. The Phenon line with a linkage distance of 25, divided samples into two large groups. These two groups were connected at a great distance, which indicates that the waters were significantly hydrogeochemically different. More mature waters with elevated mineralization were separated from the more dilute waters. Here, a Phenon line with a linkage distance of 5 was chosen, which led to 6 clusters (C1–C6).

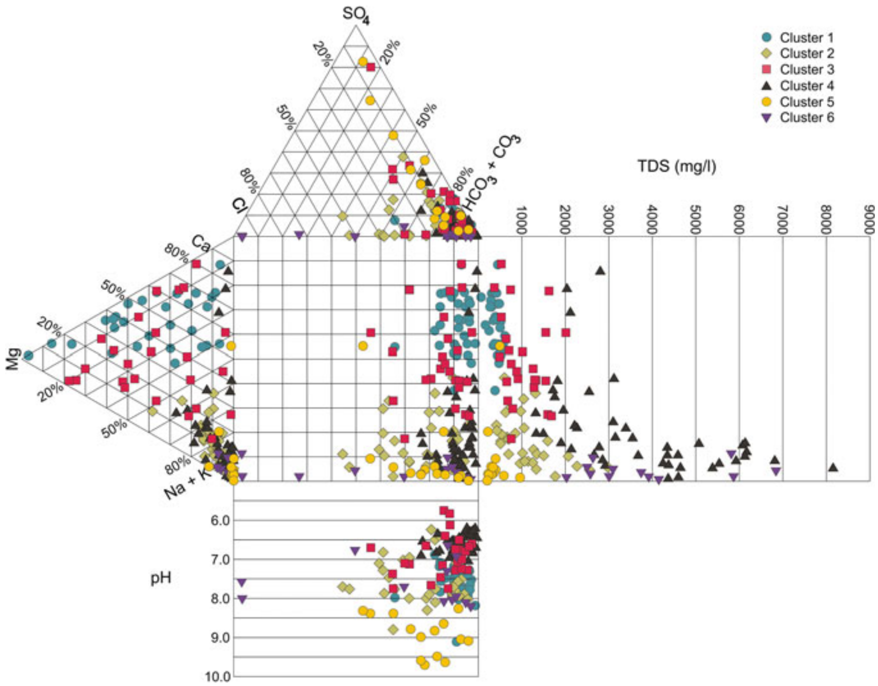

Fig. 3 Durov diagram of groundwater samples

For a clearer presentation of the results, the diagram was simplified and samples were grouped into clusters. The connecting lines correspond to the degree of similarity between clusters. As the length of the lines increases, the similarity between clusters decreases (Roques et al. 2014).

Taking into account parameters that were taken for cluster analysis, Stiff diagrams were chosen for better presentation of the parameters within clusters (Fig. 2b). The average Stiff diagram of each cluster (based on median concentrations), whose shape displays the relative proportions of major ions clearly showed the differences and similarities among clusters.

The differences between the chemical compositions of the clusters are best seen on the Durov diagram, showing the anions, cations, TDS and pH levels in parallel (Fig. 3).

Samples could be classified into three groups on the basis of total dissolved solids (TDS): low mineralized waters (C1 and C5), waters with elevated mineralization, around 1 g/L (C2 and C3) and high mineralized waters (>1 g/L, C4 and C6). When considering the temperature within the clusters, grouping was done from waters with cold to high temperatures. Median values of temperatures in C2 and C4 were below 20 °C, so these waters were not considered as thermal waters. The median temperature of samples in cluster C1 was 22 °C, which indicated the presence of cold and thermal waters. C3, C5 and C6 could be classified as thermal waters.

According to the Stiff diagram (Fig. 2b), C3, C4, C5 and C6 were quite similar on the cation and anion sides, with a domination of Na and HCO_3. C6 differed on the anion side due to a much higher concentration of Cl. C1 and C2 had different shapes on the cation side, with Ca and Mg dominating in C1 and with non-prevailing cations composition in C2.

According to pHs and redox potentials, differences between clusters were significant, which simplified the hydrogeochemical characterization of the waters. Many elements showed very large natural variations, their concentrations reflected local geological and hydrogeological settings. Hereinafter, clusters are discussed individually with attention given to trace elements, natural radionuclides and rare earth elements.

No regularity was found among the clusters in the radioactivity of mineral and thermal waters. Most samples were generally of low radioactivity. The only exceptions were slightly acidic occurrences from clusters C2 and C4.

Hydrogeochemical Characterization of Clusters

C1—Low Mineralized Water

General characteristics of the water in this cluster were low mineralization and predominance of the cations Ca and Mg and anions HCO_3. Water temperatures were in the range of 8–39.5 °C. The lowest major ion concentrations in this cluster may indicate that these waters have not had a long residence time in the aquifer. Active recharge was indicated with high redox potentials. Waters generally had low ECs, deriving from interaction with various lithologies with a prevalence of carbonates, dolomites and mafic and ultramafic rocks. Samples were generally characterized by low concentrations of trace elements and natural radioactivity.

Shallow groundwaters interacting with mafic and ultramafic rocks (usually comprising basalts, gabbros and peridotites) were generally composed of Mg–HCO_3 and high concentrations of several trace elements. For example, Cr, V and Sb exhibited elevated median concentrations in mineral waters from this cluster.

In some cases, waters originating from limestone and dolomite rocks exhibited elevated concentrations of some microelements, which suggests the potential influence of groundwater from other aquifers. Among the samples, one from the radon spa Niška Banja registered an elevated ^{226}Ra concentration (0.625 ± 0.026 Bq/L, Table 1). The spring thermal water appears along the fault, on a smashed fault zone between limestone and Miocene sediments (Nikolov et al. 2012). The high natural radiation in Niška Banja is primarily due to the presence of very high amounts of ^{226}Ra in hot spring waters. Thus, the travertine enriched by radium may represent a source of radon and may allow appropriate migration routes through its porous structure (Žunić et al. 2007).

Table 1 Minimum and maximum activities of radionuclides and gross alpha and beta activities in groundwater samples

Cluster	Parameter	α (Bq/L)	β (Bq/L)	K^{40} (Bq/L)	Ra^{228} (Bq/L)	U^{238} (Bq/L)	Ra^{226} (Bq/L)
1	MIN	<0.007	0.025 ± 0.03	0.03 ± 0.004	<0.01	<0.004	<0.008
	MAX	0.136 ± 0.016	0.256 ± 0.015	0.33 ± 0.02	<0.1	<0.7	0.625 ± 0.026
2	MIN	<0.003	<0.0535	0.06 ± 0.01	<0.01	<0.001	<0.005
	MAX	1.33 ± 0.08	1.63 ± 0.065	1.63 ± 0.08	<0.08	<0.21	2.56 ± 0.09
3	MIN	<0.009	0.052 ± 0.013	<0.058	<0.01	<0.046	<0.006
	MAX	<0.2	0.602 ± 0.07	0.59 ± 0.03	<0.06	<0.46	0.081 ± 0.008
4	MIN	<0.003	0.084 ± 0.012	0.13 ± 0.01	<0.006	<0.034	<0.01
	MAX	0.74 ± 0.16	2.82 ± 0.25	1.98 ± 0.16	0.76 ± 0.03	<0.4	0.91 ± 0.07
5	MIN	<0.006	0.018 ± 0.003	<0.012	<0.01	<0.01	<0.006
	MAX	<0.04	0.223 ± 0.014	0.27 ± 0.05	<0.12	<0.2	<0.04
6	MIN	0.087 ± 0.014	0.147 ± 0.074	<0.09	<0.04	<0.07	<0.01
	MAX	<0.26 ± 0.008	1.269 ± 0.06	0.82 ± 0.05	0.65 ± 0.03	<0.12	0.2 ± 0.01

Concentrations of REE were analyzed, classifying the lanthanides into light (LREE: La, Ce, Pr, Nd, Sm), middle (MREE: Eu, Gd, Tb, Dy) and heavy (HREE: Ho, Er, Tm, Yb, Lu) and with yttrium. Waters from this cluster were characterized by low concentrations of rare earth elements with a median of 153.85 ng/L for YREE (yttrium and REE). Median values were amongst the lowest for LREE (123.63 ng/L) and MREE (18.69 ng/L) and the highest for HREE (4.43 ng/L). When considering HREE enrichment, groundwaters reflect the combined effects of solution complexation, which stabilizes HREEs in solution, and adsorptive processes that preferentially remove positively-charged LREE species (Johannesson et al. 2005). In addition, all groundwater samples had negative Ce anomalies. These negative Ce anomalies may reflect oxidative processes occurring within the aquifer. Alternatively, they may reflect a signature inherited by reactions with the aquifer rocks (Johannesson et al. 2005). Waters also had a pronounced positive anomaly of europium.

C2—Cold Waters with Elevated TDS

C2 is a cluster of HCO_3-rich waters but with no dominating cation. Waters generally were of low temperatures with oxidizing conditions. The groundwaters were of several types according to their hydrogeochemical features. These were typically carbonic acid–enriched groundwaters with slightly acidic pH and noncarbonated waters with elevated TDS levels (around 1 g/L).

The largest numbers of occurrences were in granitoid and metamorphic rocks. Significant concentrations of Mg observed in most samples could be either related to involvement of Mg-bearing silicates within the aquifer or originating from water in contact with mafic and ultramafic rocks during the flow path. In general, median concentrations of microelements in this cluster were similar or slightly higher than in C1, which is consistent with there being several CO_2 enriched groundwater occurrences.

Several occurrences of cold carbonated waters ($t < 20$ °C) were found, characterized by elevated β-radioactivity. Natural radioactivity originates from ^{40}K which is present in acid igneous rocks. Amongst the groundwater samples in C2, one mineral spring (Cerska slatina) was marked with a high natural α-radioactivity. Cerska slatina was slightly acidic with a pH of 6.74 and with a HCO_3–Na, Ca water type, originating from an aquifer in granitoid rocks. A high content of radium isotope was found in the spring water (^{226}Ra: 2.56 ± 0.09 Bq/L) and a low concentration of ^{238}U (<0.21 Bq/L). ^{226}Ra does not necessarily indicate a high ^{238}U content, as the radium may migrate and be deposited randomly from the surrounding rock areas (Joksić et al. 2007).

Rare earth element concentrations were higher than in C1, which may reflect a favourable lithology and longer residence time. The median concentration of REEY was 218.66 ng/L. LREE had a median value of 174.82 ng/L, MREE 23.64 ng/L and HREE 31.54 ng/L. Groundwaters had slightly positive Eu and slightly negative Ce anomalies.

C3—Thermal Na–HCO_3 Waters

Elevated temperatures and electrical conductivity, reducing conditions and Na-dominant cations were the main characteristics of this cluster. The dominant components in cluster C3 were groundwaters with the highest temperatures in Serbia.

Thermal waters were characteristic for volcanogenic massives of Tertiary age (Vranjska spa 106 °C, Lukovska spa 54.7 °C, Novopazarska spa 53.6 °C) (Protić 1995).

Another significant region was Mačva, situated in the circumferential part of the Pannonian basin. Mačva lies on the parts of the Dinarides and Pannonian basin where complex tectonics are manifested by movement of a large number of smaller blocks. Deep fissures and young magmatic and plutonic bodies of Tertiary age, are of great significance for the phenomenon of thermal waters. The main aquifer consists of karstified Triassic limestone and dolomites where a water temperature of about 100 °C is expected (Martinović and Milivojević 2000). C3 also includes waters from sedimentary basins, with waters from deeper aquifers dominated by freshwater to marine-based sediments, exhibiting elevated temperature and chloride enrichment.

This cluster did not exhibit any specific features regarding the content of microelements. Occurrences with high temperatures also have elevated concentrations of Si, F, Li, B, As, etc. Gross alpha and beta activities were naturally low and in some cases below the detection limit (Table 1). REEY concentrations ranged from 43.68 to 2119.83 ng/L with a median value of 205.34 ng/L. Cluster C3 had significant MREE concentrations with a median of 51.34 ng/L. Waters had no Ce or Eu anomaly.

C4—CO_2 Rich Mineral Waters

The most important characteristics of cluster C4 were high Na, Ca and CO_2-rich waters with high EC and the lowest pHs, often with high K concentrations. The chemical composition of these groundwaters varied considerably, depending on CO_2 contents (CO_2: 271–2376 mg/L). The physico-chemical characteristics of these waters cannot be explained only by water–rock reactions, as the geochemical phenomena responsible for these features are most likely generated in deep crustal zones responsible for the high amounts of CO_2.

All occurrences were within the distribution of igneous and metamorphic crystalline rocks of regional-jointing zones. The main CO_2-generators and occurrences of carbonated groundwater in Serbia are located within the Vardar Zone that is characterized by a highly complex geological/tectonic makeup and Tertiary magmatism (Marinković et al. 2012).

The dominance of CO_2 in the gas composition resulted in the presence of elevated concentrations of major and trace elements (highest median concentrations). This group included samples with the highest concentrations of individual elements: Si (58.27 mg/L), K (113 mg/L), Li (5.72 mg/L), Rb (0.97 mg/L), Cs (0.71 mg/L), Cu (0.41 mg/L), Pb (0.013 mg/L).

High total alpha and total beta activities were present (Table 1). A large portion of the uranium and thorium in magmatic rocks is concentrated in accessory minerals such as zircon, biotite, sphene and apatite. The content of ^{226}Ra (up to 0.91 ± 0.07 Bq/L) and ^{228}Ra (up to 0.76 ± 0.03) isotopes, originating from the ^{238}U and ^{232}Th decay series, was higher in the mineral waters from C4 compared with concentrations obtained from other clusters.

Due to limitations of the analytical method in highly mineralized samples, concentrations of REEY could not be reliably detected. However, taking into account the presence of CO_2, a significant effect of weathering processes and high concentration of REEY in groundwater could be expected. The mineral and thermal waters that originated from deeper environments showed no pronounced Ce anomalies.

C5—Thermal Alkaline Waters

Waters of cluster C5 had relatively low mineralization, with Na and HCO_3 as the most common cation and anion. All of them had alkaline pHs (>8) and in most cases noticeable F and H_2S contents. The elements As, Mo and W also exhibited elevated concentrations. Water circulation through volcanic rocks can lead to formation of major hydrogeological complexes and locally to significant reservoirs of thermal waters. Waters were characterized with higher temperatures and concentrations of silica. Elevated Si content are explained by the more pronounced solubility of silicate minerals in alkaline thermal waters (Langmuir 1997). The most important thermal water in C5 was Jošanička spa with a temperature of 78 °C.

All samples belonging to C5 were characterized by low natural radioactivity and low REEY concentrations with a median of 152.26 ng/L. They had pronounced positive Ce and negative Eu anomalies. The highest concentration of REE among all samples was measured in samples taken from a spring originating from quartz–latites from the Rudnik volcanic area.

C6—Thermo-mineral Waters

Cluster C6 represents a group of mature Na–HCO_3–Cl groundwaters with high TDS (up to 17,632 mg/L) and high temperatures formed in the Pannonian basin in the Vojvodina region.

The Pannonian Basin is composed of clearly/different lithostratigraphic and structural geological units: pre-Neogene basement rocks (composed of crystal schist, magmatic and volcanic rocks and Mesozoic sediments) and sediments of Neogene and Quaternary age. The basement block structure facilitated embedment of magmatic rocks along the deeper dislocations thus forming geothermal anomalies and conditions for the accumulation of thermal waters (Protić 1995).

Sedimentation was conducted in a marine to freshwater environment, and according to such genetic zones changes in the physico-chemical composition of groundwater were expressed.

The deeper aquifers in the Pannonian basin store alkaline Na–HCO_3 thermal water, which locally can be enriched in chloride or sulphate anions. Towards the deeper parts, the residence time would be longer, with cation exchange, mixing, dissolved gas and other geochemical processes modifying the composition of water; therefore Na–HCO_3 to Na–Cl-types prevail (Szocs et al. 2013). Maximum concentrations of Na and Cl ions were 6647 and 10,209 mg/L, respectively. A long period of water-rock interaction and reducing conditions resulted in the migration of different elements into the groundwater. These conditions allowed thermal water to acquire trace elements such as B (up to 35 mg/L), Ba (up to 6 mg/L), Li (1.5 mg/L) and Sr (16 mg/L).

Elevated β-radioactivity was detected in samples with the highest salinity, while α-activity was low, even below the detection limit. Gross β-activity originated mainly from ^{40}K (from <0.09 to 0.82 ± 0.05 Bq/L), and ^{228}Ra was found to be 0.65 ± 0.03 Bq/L in one sample. Rare earth elements in thermal waters had the highest concentration in the group of MREE and yttrium, with a median value of 85.54 ng/L, with no Ce or Eu anomaly.

Conclusions

The application of HCA identified the main structural interrelationships among the physico-chemical parameters of groundwaters and enhanced similarities and dissimilarities among samples. The use of this method contributed to a new characterization of the mineral and thermal waters of Serbia, based on their hydrochemical and geological characteristics. HCA was applied to a matrix of 160 samples of groundwaters and 11 parameters, generating six clusters (C1–C6).

Low-mineralized waters with a prevalence of Ca and Mg were related to carbonate, dolomite, mafic and ultramafic rocks. Na–HCO_3 waters with low ECs were related to circulation through volcanic rocks of Tertiary age with high temperatures. Waters with higher ECs mainly reflect the geological patterns and geochemical processes (e.g. carbonate dissolution, interaction with volcanic rocks, mixing with connate water, CO_2 enrichment). Deeper aquifers formed in Neogene basins, especially the Pannonian basin, were characterized with reducing conditions and a Na–HCO_3-type and often exhibited chloride enrichment. Basement block structure facilitated the embedment of magmatic rocks along the deeper dislocations thus forming geothermal anomalies and conditions for the accumulation of waters with high temperatures.

In a strongly-faulted region in the Vardar zone composed of granitoid and crystalline rock, in particular, the origin of waters could not be determined easily by major element composition alone, as they were characterized by high mineralization and CO_2 enrichment. Temperatures of these waters could vary.

The maximum levels of trace elements (B, K, Li, Sr and Ba) were typical for the deepest aquifers characterized by long residence times for the groundwater, formed in Neogene basins, such as the Pannonian basin. Association of these elements was also characteristic of the highly-mineralized Na–HCO_3 waters with higher amounts of dissolved CO_2.

Associations of some elements clearly identified the relation with the local geological context such as As, Mo and W, related to interaction with volcanic rocks, while Cr, V and Sb were related to circulation trough mafic and ultramafic rocks.

Based on the analyzed water samples we can conclude that the elevated α- and β-activities were found mainly in waters originating from magmatic and metamorphic rocks. Natural radioactivity was mainly due to the high content of ^{40}K and naturally occurring radionuclides of the ^{238}U and ^{232}Th series. The content of ^{226}Ra and ^{228}Ra isotopes, was quite low in most samples. Water samples whose mineral contents were dominated by Ca, Mg and low TDS values did not show elevated radioactivity.

The REE data presented for thermal and mineral waters indicate that there were differences in the REE content and fractionation as a result of the interaction of groundwater with different geological materials along the flow path of the groundwater. The most significant concentrations were found in waters circulating through intermediate to acid igneous rock of Tertiary age. It is also expected to find REE enrichment in CO_2-rich waters.

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Mineral and Thermal Waters of Romania

M. Rosca, C. Bendea and A.M. Vîjdea

Abstract The search for geothermal resources for energy purposes began in the early 60s, based on a detailed geological program for hydrocarbon resources (that had extensive budgets). More than 250 wells have been drilled over the years, whose depths are between 800 and 3500 m. They revealed the presence of low-enthalpy geothermal resources (40–120 °C), which enabled the identification of many geothermal areas, most of them in the western part and three in the southern part of Romania. A recent study (involving the University of Oradea and Transgex S.A.) identified 223 wells drilled after 1965. The completion and experimental exploitation (part of geological investigations) of over 100 wells in the past 40 years enabled the evaluation of exploitable heat from geothermal reservoirs. More than 80 % of the wells are artesian producers; 68 of them (all the wells drilled in the Pannonian Basin) require anti-scaling treatment, and 4 are reinjection wells. The most comprehensive synthesis regarding the mineral and thermal waters of Romania belongs to Pricajan (Apele minerale si termale din România. Ed. Tehnica, Bucuresti, 1972) and Bandrabur et al. (Harta apelor mineral si termale din420 România, scara 1:1.000.000, Atlasul Geologic. Ministerul Geologiei, Institutul de Geologie Si421 Geofizica, Bucuresti, 1984). The work published by Pricajan (Apele minerale si termale din România. Ed. Tehnica, Bucuresti, 1972) contains a classification, from the chemical point of view, of the accumulations and occurrences of mineral waters into three major types: salted, sulfurous-sulfated and carbonated. A detailed hydrogeological description of the main accumulations of mineral waters (some of them with variable physical properties: thermalism, radioactivity), as well as their use, is also included.

Keywords Romania · Mineral water · Geothermal water

M. Rosca (✉) · C. Bendea
University of Oradea, Oradea, Romania
e-mail: mrosca@uoradea.ro

A.M. Vîjdea
Geological Institute of Romania, Bucharest, Romania

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Brief Historical Overview

In Romania, thermal springs are the only manifestations of geothermal resources. They have been witnessed since prehistoric times, but the first written proofs date back two thousand years.

The Emperor Trajan conquered Dacia at the beginning of the 2nd century, and the Romans ruled Dacia for almost two centuries. During this period, they constructed spa complexes in all localities with thermal manifestations, in order to use the natural heat and therapeutic properties of the salts and mud; moreover, some of these localities became commercially and strategically important.

The map of the Roman Empire contained the main thermal spas of Pannonia and Dacia, meaning that the spas held great balneological and military importance. Dacia had many thermal springs, of which two were well-known: Aquae and Germisara. Life of the Romans gravitated around the thermal complexes. As a result, fortresses were built in the proximity and, also, Roman legions camped in the area of Germisara. Thermal balneotherapy, however, was a local tradition long before the arrival of the Romans.

Herculane Spa is located in the southwestern part of Romania, near the Danube. After conquering Dacia, the Romans started to take advantage of the curative thermal springs in this narrow canyon of the Cerna River. It is certain, however, that these springs were used by the Dacians long before the Romans arrived. The archaeological discovery of a settlement in a cave inside the spa area indicates that people lived there throughout the Neolithic period. The Hercules *thermae* was famous for a very long period of time, even after Emperor Aurelianus left Dacia in 273 AD. In 535, the Emperor Justinianus of Constantinople set up the bishopric Ad Aquas of Dacia Ripensis (present Banat region) at Herculane Spa.

Since prehistory, the human community has lived near and developed a variety of geothermal areas: Oradea, Felix Spa, Herculane Spa, Geoagiu, Calan, Caciulata, Mangalia (Cohut and Arpasi 1995).

The mineral water springs from the Cozia–Caciulata area were first mentioned in the chronicles of Roman campaigns, and by the middle of the 19th century these waters were bottled and sold in France, being similar to the waters of some French spas (Chapelle, Eaux Bonnes, and Chatelguyon).

The first geothermal well in Romania was drilled in 1885 at Felix Spa, near Oradea. The well was 51 m deep, with a flow rate of 195 L/s and a temperature of 49 °C. This first well is still in operation. It was followed by the wells drilled at Caciulata (1893–37 °C), Oradea (1897–29 °C) and Timisoara (1902–31 °C).

The search for geothermal resources for energy purposes began in the early 60s, based on a detailed geological program for hydrocarbon resources (that had extensive budgets).

Mineral Water Resources—Characteristics and Utilization

Waters within the International Association of Hydrogeologists, *mineral water* is the type of water with a chemical composition different from that of the local underground water at its emergence point, which includes dissolved substances, in small or large amounts, or sufficiently active in order to substantially change the qualities of ordinary water. Specific components found in mineral waters are: CO_2, H_2S, HS, As, Fe, Br, I, H_2SiO_3, HBO_2, organic C, etc.

The synthesis made by Bandrabur et al. (1984), after analyzing all the materials produced up to that time, led to the development of a 1:1,000,000 scale map of mineral and thermal waters of Romania (with explanatory notes and a catalog of the main accumulations and occurrences, in tabular form). This map is part of the Geological Atlas of Romania, scale 1:1,000,000 (sheet no. 14), published by the Geological Institute of Romania, and to date remains the most comprehensive synthesis on a national scale. All maps presented in the figures within this chapter were obtained by processing the information contained in that version of the map by Geographical Information System (GIS) software.

In Romania, 138 main accumulations of mineral and thermal waters and 173 significant occurrences have been identified (Fig. 1).

The main uses include: recreation, heating, bottling plant, spa, local resort or combined use (Fig. 2).

Two main hydro-geochemical provinces have been defined: one of carbonated waters related to post-volcanic phenomena, and one of mineral waters located in

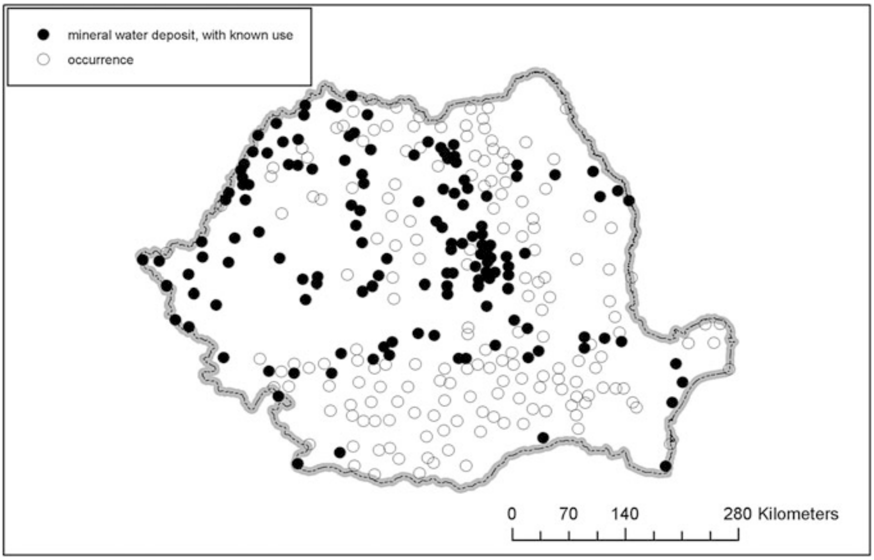

Fig. 1 Locations of mineral waters in Romania

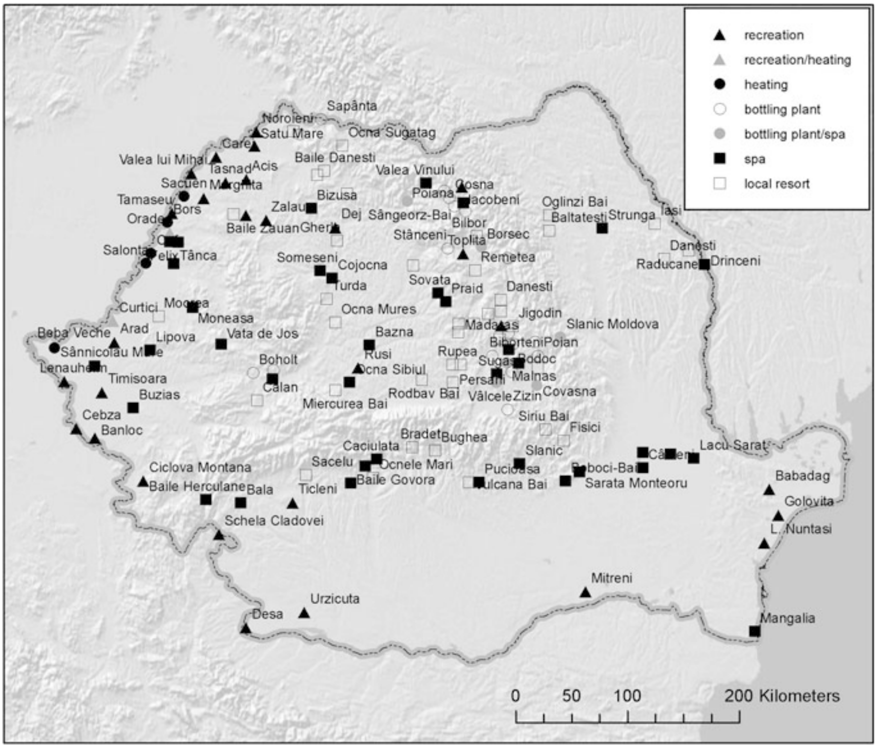

Fig. 2 Main uses of mineral waters in Romania

sedimentary basins and flysch deposits (Fig. 3). Each province is characterized by specific geological and hydrogeological conditions, occurrences of certain types of mineral and thermal waters and specific genesis. Polygons inside the provinces show areas with different vertical distribution of hydro-chemical characteristics (vertical zoning). Areas where mineral/thermal waters are missing, not yet known or occurred in a very limited number, correspond mainlyto Apuseni Mts., Southern Carpathians and Dobrogea.

The origin of the waters was determined based on the geological and hydro-geological conditions of the mineral water reservoirs, the specific chemical composition, the content of chlorine, and the Cl/Br ratio. The water origin is quite different in the two provinces: atmospheric, atmospheric with marine intake, and marine with atmospheric intake (Fig. 4).

Gases dissolved in the mineral waters are of a magmatic origin in the first province (CO_2), and atmospheric (N_2, O_2) or/and bio-chemical origin (CH_4, CH_4–N_2, CH_4–N_2–CO_2,CH_4–N_2–H_2S) in the second province (Fig. 5). The hydro-chemical type of the mineral waters was determined based on the anions and cations present in an amount of at least 20 %, independently of the sum of total anions and cations.

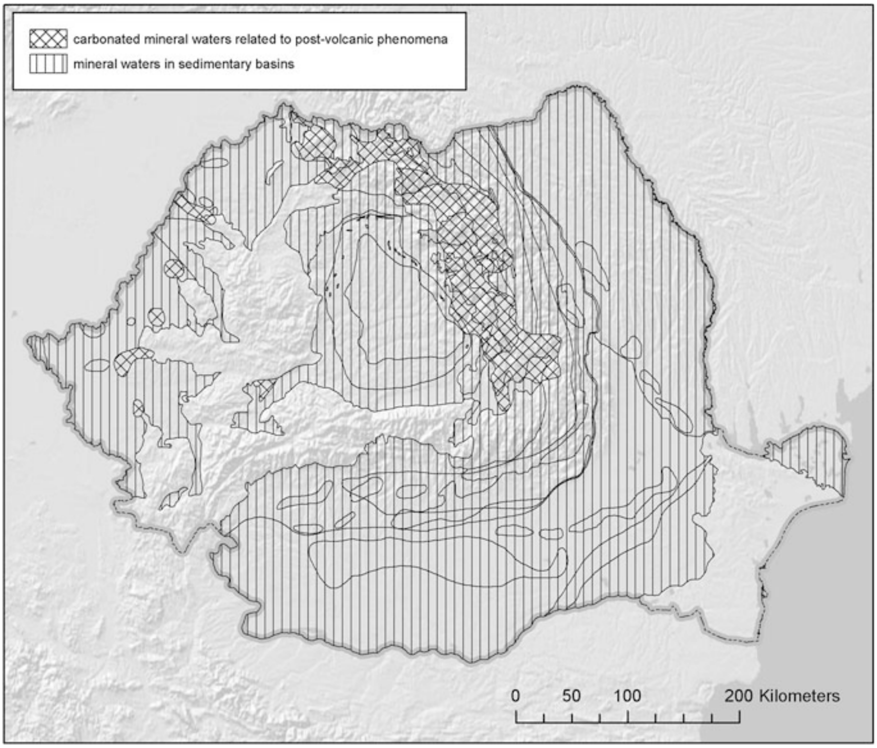

Fig. 3 Hydrogeochemical provinces of Romania

In the first hydro-geochemical province, the distribution of anions (Cl^-, HCO_3^-, SO_4^{2-}) highlights the presence of HCO_3^- in the entire hydro-chemical profile or in the upper part, while in the second province Cl^- dominates (Fig. 6). The distribution of cations (Na^+, Ca^{2+}, Mg^{2+}) indicates the overall spread of Na^+ and the dominance of Na^+ and Ca^{2+} in the second hydro-chemical province, in the sedimentary regions of the Moldavian Platform in the east, the Moesic Platform in the south, the Pannonian Depression in the west and the Transylvania Depression in the center (Fig. 7). Mg^{2+} characterizes the upper part of the profile in the first hydro-chemical province, with carbonated waters related to post-volcanic phenomena.

Consequently, in the first hydro-chemical province, within the area of mofette haloes, the waters are carbonated, carbonated–chlorinated and chlorinated, rich in calcium, magnesium and sodium. The mineralization is generally up to 5 g/L, and can reach 35 g/L at the bottom of the hydro-geochemical profile (Fig. 8).

In the second province, related to the sedimentary basins and flysch deposits, in the upper part of the profile the waters are carbonated or calcium/sodium sulfated, sometimes with H_2S. The mineralization is usually up to 5 g/L, rarely up to 15 g/L.

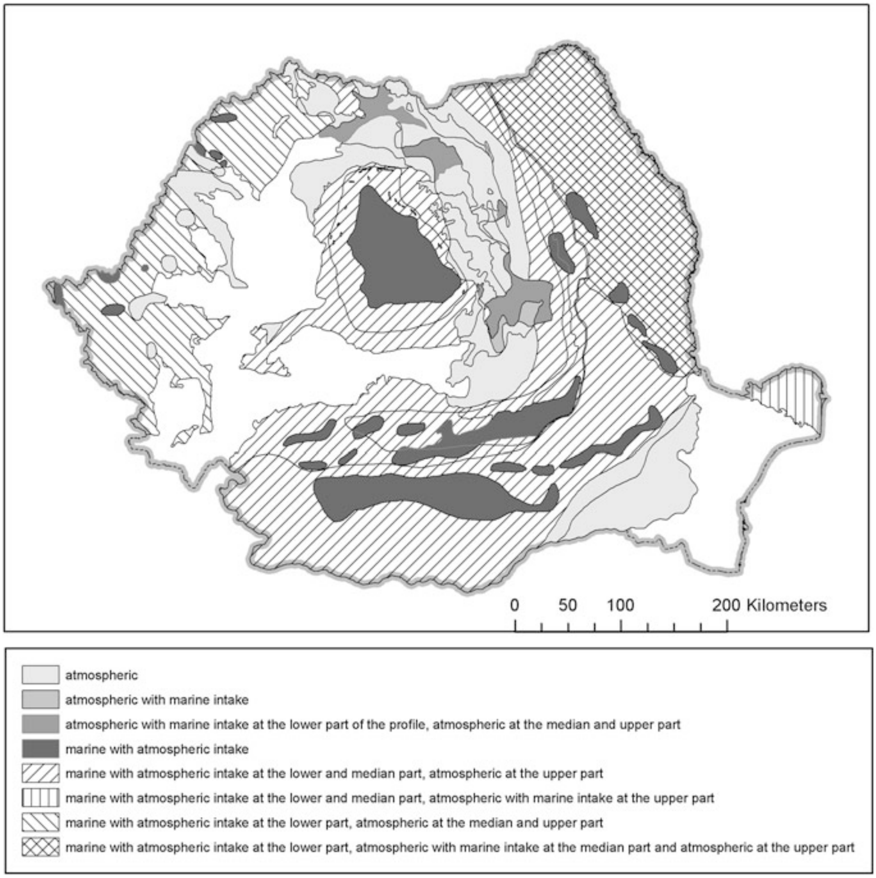

Fig. 4 Origin of mineral waters in Romania

The median and lower parts of the profile are characterized by sodium–chlorinated waters, with a mineralization growing from 10 up to 150 g/L or even 350 g/L.

Mineral waters rich in some specific components, like Br, I, H_2S, are located in the Moldavian Platform, the Moesian Platform, the Danube Delta and the Transylvania Depression (Fig. 9). Mineral waters with temperatures higher than 35 °C are found in the western part of Romania, in the Pannonian Depression, in the eastern part, in the Moldavian Platform, in the south, in the Moesian Platform, and in a small area in the center, in the Transylvania Depression (Fig. 10).

Three main types of mineral waters can be defined from the chemical and genesis points of view (Pricajan 1972): salted, sulfurous-sulfated and carbonated. Depending on the nature of the locally levigated rocks, some secondary hydro-chemical characters may occur due to the presence of iron, arsenic, potassium, calcium, magnesium, chlorine, etc. The majority of natural mineral waters

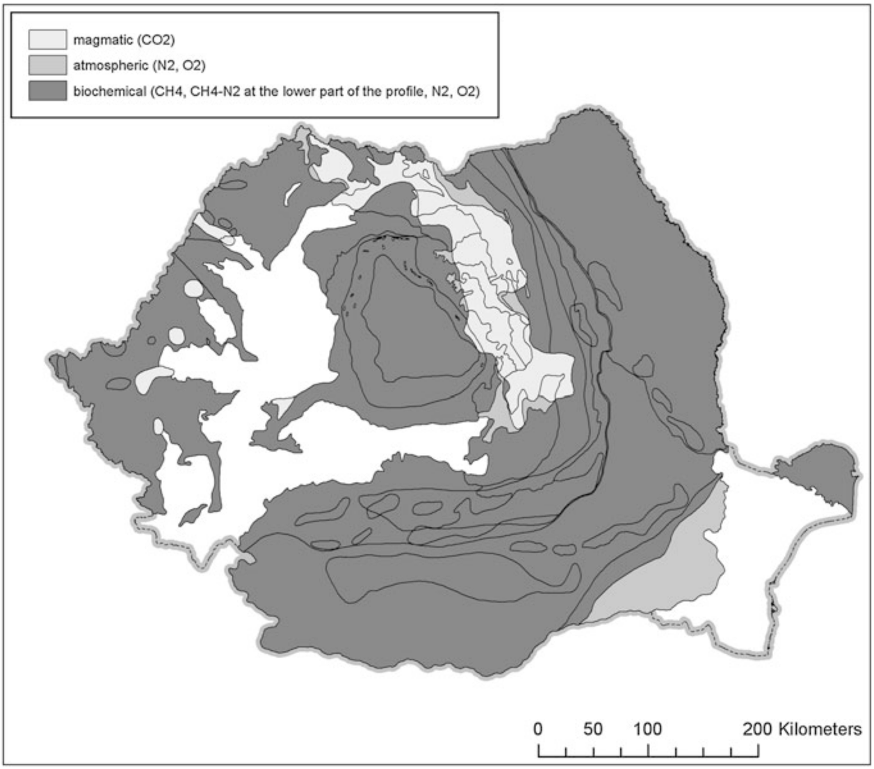

Fig. 5 Origin of gases contained in mineral waters in Romania

bottled in Romania are calcium–hydrogen-carbonated, with secondary characters given by magnesium or sodium.

With regard to these waters, carbon dioxide is genetically linked to the presence of intrusive rocks in the areas with active volcanoes in the geologic past, in zones with post-volcanic phenomena (mofette). Carbon dioxide in gaseous form migrates to the surface through cracks. In the collector rock, carbon dioxide is dissolved in water, giving it an increased aggressiveness. In this case, the water mineralization is more intense. That is why carbonated natural mineral waters are usually heavily mineralized.

There are four main areas of occurrence of hydro-carbonated water: three areas within the mofette halo of volcanic rocks in the Oaș–Gutâi–Țibleș Mts., the Călimani–Harghita Mts. and the Apuseni Mts., and one area related to deep intrusive bodies in the Pannonian Depression. The carbonated character comes from incorporating the carbon dioxide encountered during underground movement. The interception of carbon dioxide can occur at different depths but always along tectonic accidents, which facilitate upward movement and lateral diffusion over a distance of tens of kilometers.

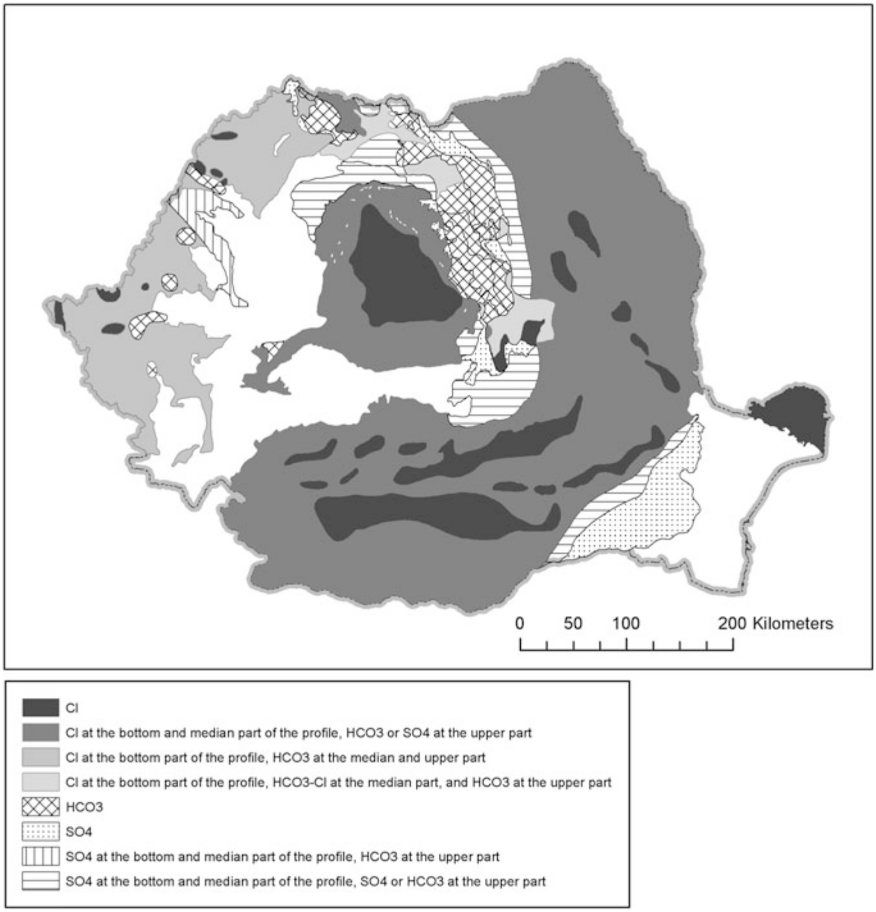

Fig. 6 Distribution of anions in mineral waters of Romania

The chemical nature of the waters is determined by the nature and composition of the rocks into which they levigate, both in their upward and downward movement. This process generates mineral waters with specific and sometimes complex chemical compositions, such as: acid-carbon (arsenical, ferruginous) chlorine–sodic, calcium–carbonated, sometimes sulfurous in Miocene flysch formations, and acid carbonic in crystalline rocks.

Salted mineral waters are hyper-chlorinated waters (where sodium is the prevailing element) and may also contain, in exceptional cases, bromine, potassium, boron, and iodine, in large amounts, depending on the geological formations where they are found. They have a high concentration of total dissolved salts and are widespread in the country (over 40,000 km^2), being located at different depths.

Depending on the manner in which mineralization occurs, salted waters are related to the genesis of hydrocarbons and may also be contaminated with reservoir

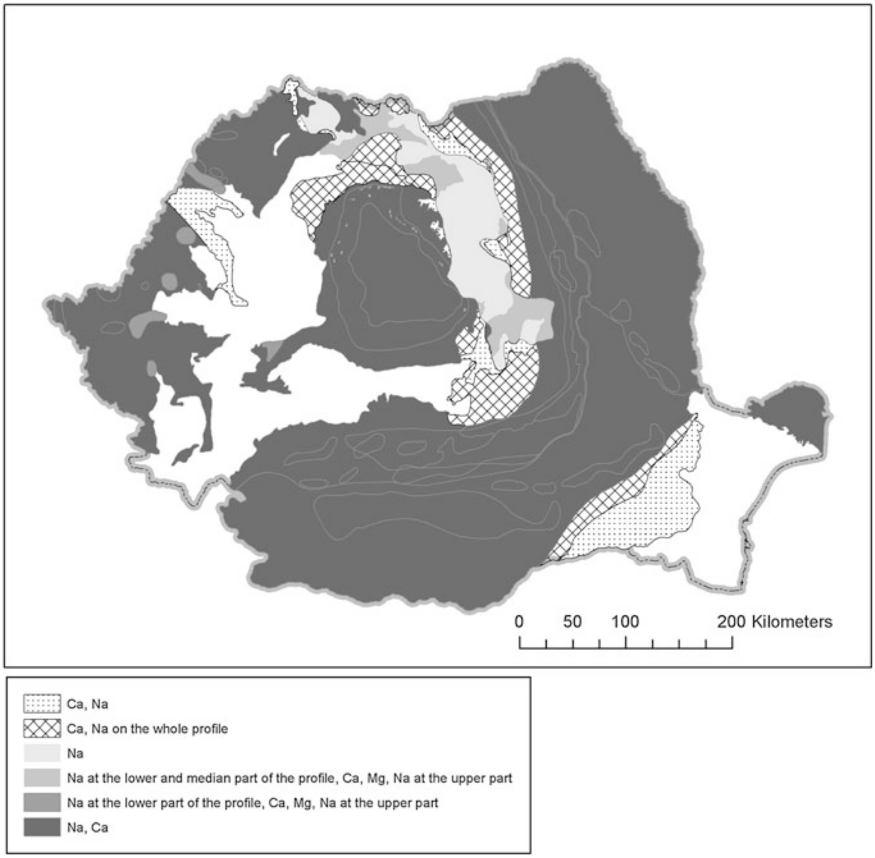

Fig. 7 Distribution of cations in mineral waters of Romania

water. These waters occur in the second hydro-chemical province, both inside and outside the Carpathian arch, in the flysch area of the Eastern Carpathians, in the Miocene formations of the Eastern Carpathians, as well as in the Getic, Valachian, Pannonian and Transylvania depressions (in the latest case accompanying gas fields).

Other salted waters are formed by the action of surficial waters, which are directly washing the salt massifs or residual salts of the outcrops of shallow salt deposits in Maramures and Transylvania depressions, in the Miocene formations of the Getic Depression (usually accompanying diapirs at Slanic Prahova, Govora, Bazna) and of the Eastern Carpathians and the Moldavian Platform. Salted waters formed in this way can also be found in Quaternary deposits, located directly on the salt deposits or salt-breccia deposits of the Romanian Plain (e.g. the salty Amara Lake) and in the Danube Delta (the phreatic waters confined in the sands of marine origin of the Razelm–Sinoe complex lagunar system and Murighiol Lake).

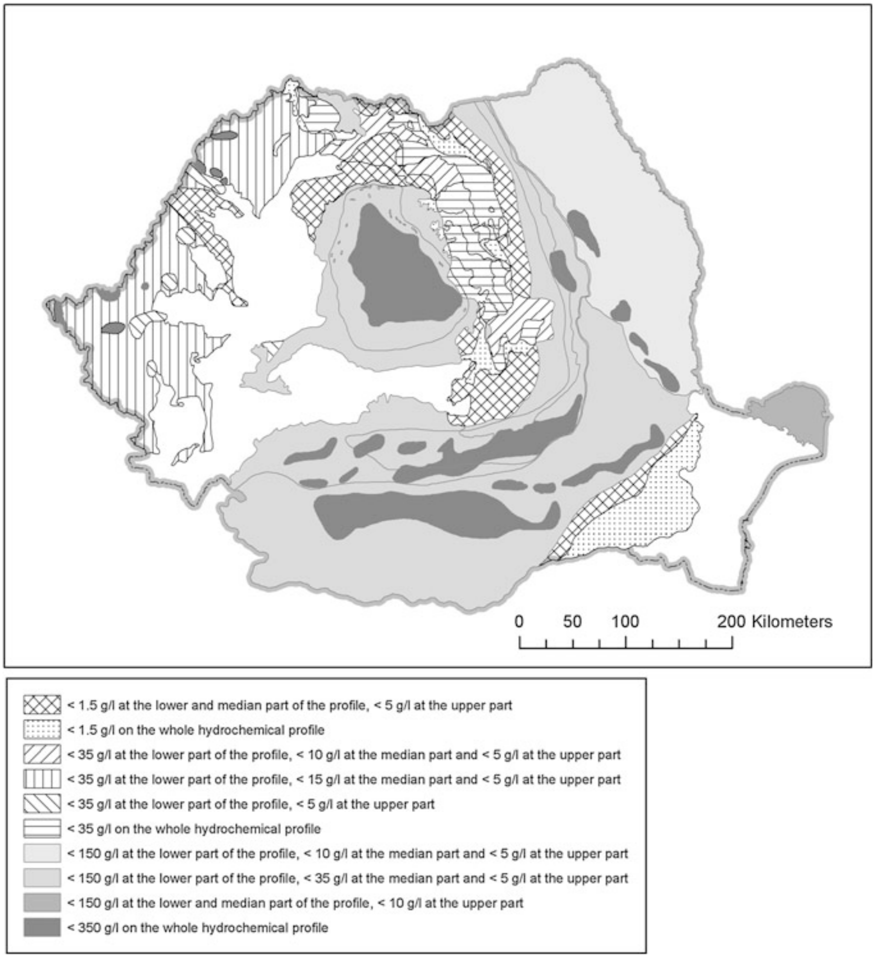

Fig. 8 Vertical zoning of mineralization in the hydrogeochemical provinces of Romania

Mineralization may also occur through the leaching of salt deposits by underground water at greater depths, leading to chlorine–magnesium or chlorine–calcium waters. The chlorine–sulfur or chlorine–carbonated salted waters of higher depths occur naturally along the faults and fractures of marl and clay complexes or in the permeable intercalations of the Miocene pelites, created by capillarity drainage conditions in permeable levels. In exceptional cases the waters can contain large amounts of potassium and bromine, as in the Miocene formations of the Eastern Carpathians and the Transylvania Depression.

The third category of mineral waters, sulfurous and sulfate waters, have a narrower spread than the other two types, and are characterized by the presence of titratable sulfur in water of at least 1 mg/L. It can result from the sulfate reduction by the action of sulfurous bacteria or organic substances, or from leaching of

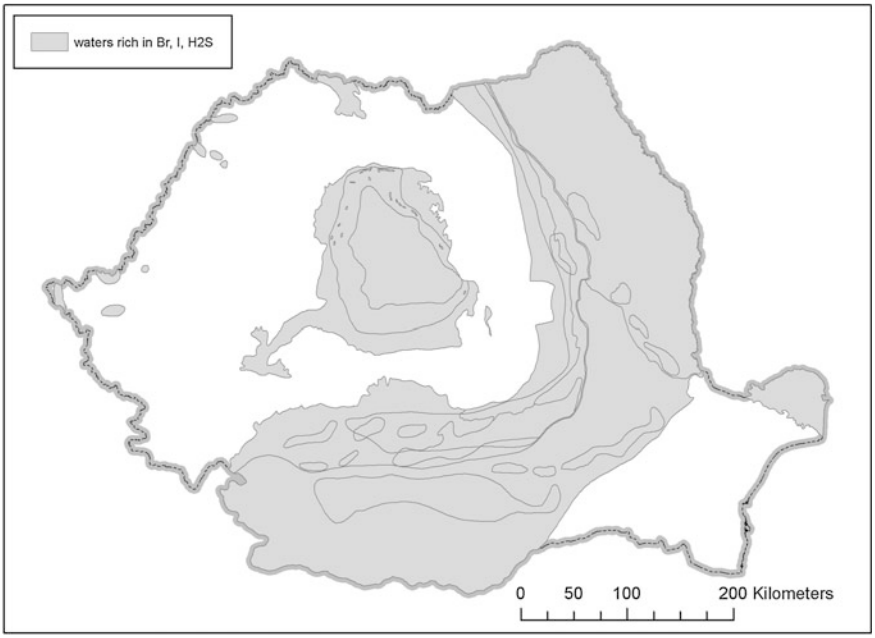

Fig. 9 Distribution of specific components in mineral waters (Br, I, H_2S) of Romania

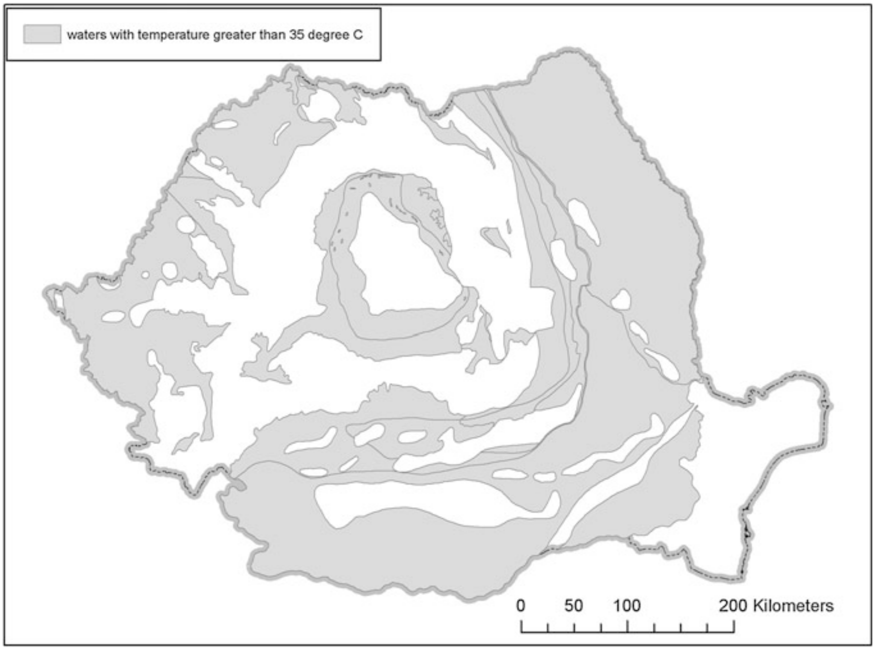

Fig. 10 Distribution of specific components in mineral waters (› 35 °C) of Romania

sulfides in sedimentary rocks or coal beds. Sometimes these waters occur by simply dissolving gypsum (Buda–Teşcani sulfated mineralized waters).

Simple sulfurous waters are rare (Mangalia, Sinaia), while very often sulfurous waters contain alkali or alkaline-earth metals (Căciulata–Călimăneşti).

Sodium–chlorinated sulfurous waters can be found at Călimăneşti, Băile Govora, Nicolina, Săcelu, Vizantea. At Herculane Spa, thermal sulfurous waters are used in external treatment. At Pucioasa, the groundwater directly washes the Miocene gypsum, leading to a sulfurous water source.

At present, in Romania there are 122 exploitation licenses for mineral waters, of which 8 for thermo-mineral waters and 42 for geothermal waters. The interest in this natural resource is great, so that another 32 licenses for exploration have been granted, of which 17 for geothermal waters (http://www.namr.ro/minning-law/working-licenses-permits/).

Thermal Water Resources—Characteristics and Utilization

The geothermal systems discovered on the Romanian territory are located in porous permeable formations such as Pannonian sandstone, interbedded with clays and shales specific of the Western Plain, and Senonian specific of the Olt Valley. Some geothermal systems are located in carbonate formations of Triassic age in the basement of the Pannonian Basin, and of Malm–Aptian age in the Moesian Platform (Fig. 11).

Fig. 11 Locations of the main Romanian geothermal reservoirs. Reproduced from Cohut and Bendea (2000)

The Pannonian geothermal aquifer is multi-layered, confined and located in sandstones at the basement of the Upper Pannonian (late Neocene age), over an approximate area of 2500 km^2 along the western border of Romania, from Satu Mare in the north to Timisoara and Jimbolia in the south. The aquifer is situated at a depth of 800–2400 m. It was investigated by means of more than 100 geothermal wells, all possible producers, of which 33 are currently exploited. The thermal gradient is 45–55 °C/km. Well head temperatures range between 50 and 85 °C. The mineralization (TDS) of the geothermal waters is 4–5 g/L (sodium–bicarbonate–chloride type) and most of the waters shows carbonate scaling, prevented by downhole chemical inhibition. Combustible gases, mainly methane, are separated from the geothermal water and not used (yet). The wells are mainly artesian; very few have downhole pumps.

The main geothermal areas, north to south, are: Satu Mare, Tasnad, Acas, Marghita, Sacuieni, Salonta, Curtici–Macea–Dorobanti, Nadlac, Lovrin, Tomnatic, Sannicolau Mare, Jimbolia and Timisoara. The main uses are: heating of 10 hectares of greenhouses; district heating for about 2500 flats; and sanitary hot water supply for 2200 flats, health and recreational bathing, and fish farming. Other users, such as for ceramics drying, timber drying, and hemp and flax processing, went out of business.

The Oradea geothermal reservoir is located in Triassic limestones and dolomites at depths of 2200–3200 m, over an area of about 75 km^2. It is exploited by 14 wells with a total maximum flow rate of 140 L/s of geothermal water with well head temperatures of 70–105 °C. There are no dissolved gases and the mineralization is 0.9–1.2 g/L; the water is of calcium–sulfate–bicarbonate type. The Oradea Triassic aquifer is hydrodynamically connected to the Felix Spa Cretaceous aquifer; together they are part of the active natural flow of water. The water is about 20,000 years old and the recharge area is in the northern edge of the Padurea Craiului Mountains and the Borod Basin. Although there is significant recharge of the geothermal system, the exploitation with a total flow rate of over 300 L/s generates a pressure drawdown in the system that is prevented by reinjection. Reinjection is the result of successful completion and beginning of operation of the first doublet in Nufarul District, Oradea City, in October 1992. The Felix Spa reservoir is currently exploited by more than ten wells, with depths between 50 and 450 m. The total flow rate available from these wells is 210 L/s. The geothermal water has wellhead temperatures of 36–48 °C and is potable. The annual utilization of geothermal energy in Oradea represents about 30 % of the total geothermal heat produced in Romania.

The Bors geothermal reservoir is situated about 6 km northwest of Oradea. This reservoir is completely different from the Oradea reservoir, although both are located in fissured carbonate formations. The Bors reservoir is a tectonically closed aquifer, with a small surface area of 12 km^2. The geothermal water has 13 g/L of total dissolved salts (TDS), 5 Nm^3/m^3 gas-water ratio (GWR), and a high scaling potential, prevented by chemical inhibition. The dissolved gasses are 70 % CO_2 and 30 % CH_4. The reservoir temperature is higher than 130 °C at the average depth of 2500 m. The artesian production of the wells could only be maintained by reinjecting the whole amount of extracted geothermal water, and of colder water from shallower wells during the summer. In the past, three wells were used to produce a total flow rate of 50 L/s, and two other wells were used for reinjection, at a pressure that did not exceed 6 bar. The geothermal water was used for heating 12 ha of greenhouses (now out of business). The dissolved gases were partially separated at 7 bar, which was the operating pressure, and then the fluid was passed through heat exchangers before being reinjected. The installed power was about 8 MW_t, and the annual energy savings were about 3000 TOE/y. This reservoir is currently not exploited at all. In January 2014, Transgex S.A. restarted production from one well, supplying the primary heating agent to two commercial companies in the area (about 17 TJ/y.).

The Beius geothermal reservoir is situated about 60 km southeast of Oradea. The reservoir is located in fissured Triassic calcite and dolomite, 1870–2370 m deep. The first well was drilled in 1996, down to 2576 m. A line shaft pump was installed in the well in 1999, now producing up to 45 L/s of geothermal water with an 83 °C wellhead temperature. A second well was drilled in early 2004; a line shaft pump was installed later that year and can also produce up to 45 L/s of geothermal water with an 85 °C wellhead temperature. A third well was drilled in 2010 and is used to reinject heat-depleted geothermal water from closed-loop systems. The geothermal water from the two production wells has a low mineralization (462 mg/L TDS), and 22.13 mg/L of non-condensable gases (NCG), mainly CO_2 and 0.01 mg/L of H_2S. The geothermal water from both wells is currently used to supply district heating to a part of the town of Beius (for a district heating system with 10 substations supplying a block of flats, two hospitals, two schools, public buildings, heating systems of many individual houses in open loop, swimming pool, etc.).

The Ciumeghiu geothermal reservoir is also located in the Western Plain, 50 km south to Oradea. The geothermal water has a wellhead temperature of 105 °C and high mineralization (5–6 g/L TDS), with a strong carbonate scaling potential (prevented by chemical inhibition at a depth of 400 m). The aquifer is located in Lower Pannonian gritstone, at an average depth of 2200 m. The main dissolved gas is CH_4, and GWR is 3 Nm^3/m^3. The reservoir was investigated by means of 4 wells, but only one was in use (until the greenhouses in the area were closed), with a capacity of 5 MW_t (of which 1 MW_t from separated combustible gases). The geothermal water was used to heat greenhouses (now out of business).

The Cozia-Calimanesti geothermal reservoir (Olt Valley) produces artesian geothermal water, with flow rates between 8.5 and 22 L/s, and shut-in wellhead pressures of 30–33 bar, from fissured siltstones of Senonian age. The reservoir depth is 2700–3250 m, the wellhead temperature 70–95 °C, and TDS 15.7 g/L; there is no major scaling (only minor deposition and some corrosion have been observed in the years of operation). GWR is 1–2.0 Nm^3/m^3 (90 % methane). Although the reservoir has been exploited for more than 25 years, there is no interference between the wells and no significant pressure drawdown. The thermal potential achievable from the 4 wells is about 14 MW_t (of which 3.5 MW_t from combustible gases—if used), but only about 7 MW_t is used at present. The energy equivalent gained in this way is 3500 TOE/y. The geothermal water is mainly used for district heating (2250 equivalent flats), and for health and recreational bathing.

The Otopeni geothermal reservoir is located north of Bucharest. It is only partially delimited (about 300 km^2). The 23 drilled wells (of which only 17 potential producers or injectors) show a huge aquifer located in fissured limestone and dolomites, situated at a depth of 2000–3200 m, belonging to the Moesian Platform. The geothermal water has wellhead temperatures of 58–84 °C, and a rather high TDS (1.5–2.2 g/L), with a high H_2S content (up to 30 ppm). Therefore, reinjection is compulsory for environmental protection. Production was carried out in the Otopeni area using downhole pumps, because the water level in the wells is at 80 m below surface. The total flow rate was 22–28 L/s. At present, only one well is in use, almost all year round, for health and recreational bathing.

Relevant Legislation

At present, Romanian legislation is harmonized with European Union principles and supports renewable energy sources, geothermal being specifically mentioned.

The Kyoto objectives imply for the European Union, between 2008 and 2012, a reduction by 8 % of greenhouse gas emissions, compared to the 1990 level (corresponding to about 600 million tons per year of CO_2 equivalent). The European Renewable Energy Roadmap adopted in 2007, which defines clear targets and goals to reach a 20 % contribution of renewable energy to the energy mix by the year 2020, has also been adopted by Romania and included in the Energy Strategy for the 2007–2020 period. These targets are also mandatory for Romania, after joining the European Union in 2007.

Underground mineral resources are owned by the State. The Romanian Constitution, adopted in 1991, stipulates that "resources of any nature occurring in the underground, [and] the water with a useful energy content, etc., are exclusively public property". Mineral rights are excluded from private ownership. Their exploration and exploitation are regulated by the Mining Law (No. 61/1998, old version, modified by Law no. 85/2003).

Obtaining concession licenses (from the National Agency for Mineral Resources, see below) for exploration and exploitation was regulated by the Concession Law No. 219/1998 until 2006, when it was replaced by Law 22/2007.

The Environment Protection Law (No. 137/1995 old version, modified by Law No. 265/2006), stipulates that the activity of drilling wells for underground fluid production is subject to an environmental authorization procedure. Only water wells for domestic use (residential areas, family houses) with depths of less than 50 m are excepted from this procedure. Wells for (vertical loop) borehole heat exchangers are not specifically mentioned (this is still an unusual technical solution in Romania, most ground source heat exchangers are horizontal, being less expensive).

The Water Law (No. 107/1996, old version, modified by Law No. 310/2004) regulates the use and protection of Romania's water resources. All waters—surface and underground—belong to the state. They can be used freely for drinking, washing, irrigation and other needs, even in small installations, but cannot be sold. Otherwise, the right to use either surface water or groundwater is subject of authorization. In order to stimulate the development of small and medium enterprises, Law No. 346/2004 stipulates that for some small-size works and activities (flow rates below 36 m^3/h), a notification to the Competent Authority is sufficient.

The Thermal Energy Law No. 325/2006 sets the general rules for district heating systems and is intended to stimulate the use of renewable energy sources, among which geothermal is specifically mentioned. According to this law, all district heating systems have to be public property, but operation can be licensed to a specialized private company or to a public-private joint venture. The district heating company purchases heat from any producer (public or private), transports, distributes and supplies it to consumers.

The Law on the Promotion of Energy Production from Renewable Energy Sources (old version No. 220/2008, modified by Law No. 134/2012) regulates all aspects regarding the "green certificates" issued for electric energy produced from renewable energy sources, geothermal included. For 1 MWh of electric energy produced from geothermal energy the producer now receives 2 green certificates. One additional green certificate is awarded for co-generation systems. Unfortunately, the National Agency for Energy Regulation does not award, yet, any green certificates for geothermal power, claiming that there are too few producers and not enough information to notify the European Commission. Some restrictions apply, different for certain renewable energy sources, mainly as minimum or maximum installed capacity and first year of operation. The green certificates can be sold on the Green Certificates Exchange. The minimum and maximum prices for one green certificate are set by the government each year. In 2014, the minimum price was 30 € and the maximum 60 €. Producers of energy from fossil fuels have annual quotas of green certificates they have to acquire, as a function of their annual energy production. Otherwise, they have to pay a fine. These quotas are fixed for each year until 2020, and increase every year. As the available green certificates are far below the demand, their selling price is usually the maximum set for each year. At the end of the year, the money collected from fines is distributed to the green energy producers, proportional to the number of green certificates they sold, providing additional income, on top of that from the certificates.

The National Agency for Mineral Resources (NAMR), established in 1993, is the regulatory authority that administers mineral resources, as well as the competent authority which coordinates mining operations under the Mining Law, according to the provisions of the Concession Law. In particular, the Agency is authorized to institute hydro-geological protection perimeters, for underground waters (mineral and thermo-mineral), to negotiate the terms and conclude agreements for the exploration and production of mineral resources, and to select, finance, and follow up on all geological exploration and exploitation works for geothermal resources.

Order No. 97/20.05.2008 of the President of NAMR on the technical instructions for classifying and assessing the resources/reserves of natural mineral water, therapeutic mineral water, geothermal water, gases that accompany them, and noncombustible gases defines all these mineral resources, and geothermal waters are defined as “a renewable useful mineral substance, represented by the totality of underground water which have the role of transporting heat from the terrestrial crust, used for energy or as therapeutic mineral water, with temperatures at the source higher than 20 °C”.

The National Agency for Environment Protection, established by Governmental Decision no. 1625/23.12.2003, is the responsible authority under the Environment Protection Law. Its intended duty is to ensure a healthy environment, in line with Romania’s economic development and social progress. Its mission consists of ensuring a better environment for the present and future generations, through continuous enhancement of air, soil and water quality.

The National Administration “Romanian Waters” is the competent authority under the Water Law. Its competence extends to surface waters in the public domain, as regulated by the Law of Waters, with their minor beds, shorelines and lake basins, as well as their natural resources and energy potential, underground waters, sea-walls and beaches, dams, reservoirs and others (Rosca 2009).

The economic and technical operation and development of the energy sector (electric and thermal) is regulated, administered, supervised and monitored by the National Agency for Energy Regulation (NAER), which was set up by an emergency ordinance in October 1998 as an independent and autonomous public institution. For electric energy, according to the current legislation, the National Power Transport Company (TRANSELECTRICA) has to purchase the entire available power produced from renewable resources at the price established by the NAER, based on a financial and economic assessment study. The competent authority for the Energy Efficiency Law was the National Agency for Energy Conservation (NAEC), which was included in NAER.

For thermal energy sold to a private commercial customer, the unit selling price is usually fixed by direct negotiation between the two parties. In case the customer is a public utility (e.g. district heating), the unit selling price has to be approved by the Local Council and also by the National Regulatory Agency for Local Administration.

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Thermal Waters of Albania

Romeo Eftimi and Alfred Frashëri

Abstract Albania is a small country but its regional hydrogeological picture is very heterogeneous. The complex geological-structural and geomorphological conditions of Albania have resulted in the formation of diverse aquifers with regard to their hydraulic type, resources, hydrodynamics and hydrochemical characteristics. Among them there are some deep aquifers associated with different rocks like evaporate, carbonate and molasse, hosting thermal waters. Based on geological conditions, as well as hydrochemical and thermal characteristics, four hydrochemical water types and four related provinces of thermal waters are distinguished in Albania. H_2S, SO_4–Ca-type waters (temperature 43 °C) originate from evaporite rocks of the Korab Province. Samples of the Cl–Na–Ca or Cl–SO_4–Na–Ca-type, of varying temperatures and H_2S concentrations, originate from deep–lying limestone–dolomite anticline structures of the Kruja Province. Most samples from the Pre-Adriatic Depression Province related to deep-laying Neogene, mainly Tortonian, sandstone aquifers are of the Na–Cl water type with H_2S and CH_4 gases and usually with high Br and J concentrations. A few water samples from the Ionian Province are of the Cl–Na water-type and measure varying temperatures. For each province the geological–structural, thermal and hydrochemical characteristics are described in the paper. The richest province in terms of thermal water resources is the Kruja Province, where most of the warm and hot thermal H_2S springs are located.

Keywords Thermal water · Regionalization of thermal waters · Geothermometry · Albania

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R. Eftimi (✉)
Rr. Rreshit Collaku, Pll. Eurocol, nr 43, Tirana, Albania
e-mail: eftimiromeo@gmail.com

A. Frashëri
Faculty of Geology and Mining, Tirana, Albania

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Introduction

In Albania, the presence of high mountain chains and active fault systems favors the rise of deep waters that discharge at the surface as thermomineral springs. A number of important thermal springs rich in H_2S, mostly located in the Kruja tectonic zone, rise from deep karst aquifers related to buried anticline carbonate structures. Important thermal water resources have also been explored by many deep oil and gas wells. Some thermal springs, like Peshkopi, Llixh Elbasan and Leskoviku, and the deep wells of Bilaj and Kozan, are widely used for balneotherapy due to their excellent curative properties.

The first noteworthy investigation of thermal waters in Albania was undertaken by Avgustinski et al. (1957). That study presented detailed chemical analyses of most thermal springs and some free-flowing deep wells, and proposed a regionalization of thermal water types of Albania. Subsequent investigations were partial and do not represent major contributions to this field. Some important data about thermal waters (simple chemical analyses and some water temperature measurements) have been collected from deep oil and gas exploration wells. Based on the data on deep wells, the hydrochemical characteristics of deep groundwaters were summarized by Shtrepi (1971, 1972). He drew an important conclusion about the hydrochemical inversion of deep groundwater in the Peri-Adriatic Depression (Shtrepi 1980). The effect of evaporate tectonics on the development of regional faulting and the formation of thermal waters of the Kruja zone was described by Velaj (1995, 1999, 2002).

Studies on the geothermal field and an evaluation of geothermal energy in Albania were carried out during the preparation of the Atlas of Geothermal Resources in Albania. The temperature, average geothermal gradient, heat flow density and geothermal zone maps were produced from the data, at the depths of 100, 500, 1000, 2000 and 3000 m below the surface (Frashëri et al. 2004).

The goal of this paper is to summarize existing data on thermal groundwater, in close relation to the geological-tectonic construction of Albania, as part of the deep regional groundwater flow system, and the thermal springs as their discharge features.

Geological Setting of the Albanides

The Albanides represent an assemblage of geological structures in the territory of Albania, as part of the southern branch of the Mediterranean Alpine Belt (Fig. 1). Two major peleogeographic domains comprise the Albanides: *Internal Albanides* and *External Albanides* (Aubouen and Ndoja 1964; Papa 1993; Meço and Aliaj 2000; Xhomo et al. 2002). Internal Albanides are characterized by the presence of an intensively tectonized ophiolitic belt, and External Albanides are part of the South Adriatic sedimentary basin and are affected only by the late Miocene tectonic stages. The Earth's crust in the Albanides is interrupted by a system of longitudinal

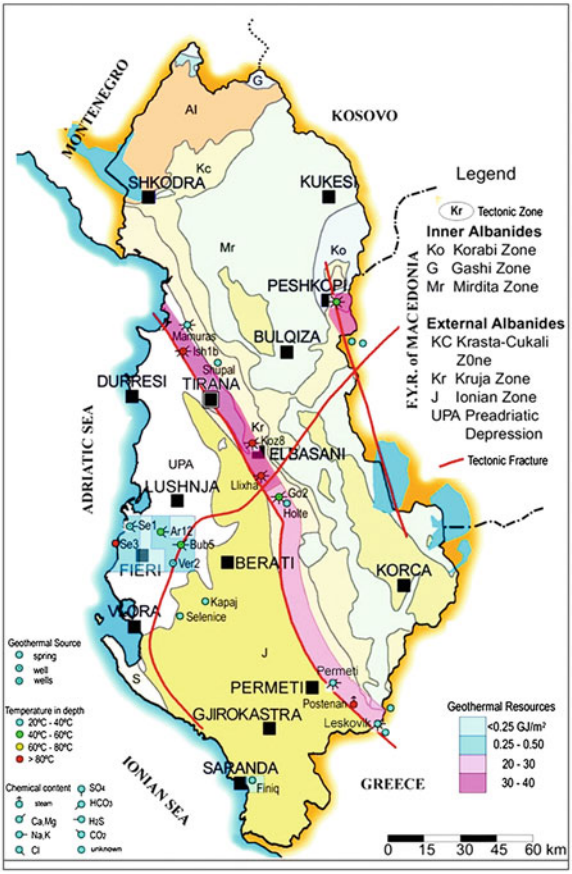


Fig. 1 Thermal springs and geothermal resources of Albania (Frashëri et al. 2004)

faults of NW–SE direction and some transversal faults that even touch the mantle (Aliaj 1989; Frashëri et al. 2003).

The tectonic zones of the *Internal Albanides* extend in the eastern part of Albania (Fig. 1). The *Korabi Zone* continues into the Golia Zone in the Dinarides and the Pelagonian Zone in the Hellenides, and is generally represented by Paleozoic terrigene metamorphic rocks (Meço and Aliaj 2000; Xhomo et al. 2002). The *Mirdita Zone* continues as the Serbian Zone in the Dinarides and the Subpelagonian Zone in the Hellenides. The lower tectonic unit of the Mirdita Zone is presented by an allochthonous ophiolitic belt (2–14 km thick), overthrown onto the formation of the Krasta–Cukali Zone of the External Albanides (Meço and Aliaj 2000; Xhomo et al. 2002). During later tectonic-neotectonic stages, Neogene molasse was deposited in the Korça-Librazhd and Burrel inner depressions. The *Gashi Zone* continues as the Durmitori Zone of the Dinarides and consists of metamorphic and terrigene rocks, limestone and volcanic rocks.

The tectonic zones of the *External Albanides* extend in western part of Albania (Fig. 1). The *Alps Zone* is analogous to the High Karst in the Dinarides and the

Parnas Zone in the Hellenides. The oldest rocks that outcrop within this zone are Permian sandstones and conglomerates. Most of the Albanian Alps consist mainly of Mesozoic limestone forming some monoclines, combined with smaller anticlines. The *Krasta–Cukali Zone* is analogous to the Budva Zone of the Dinarides and the Pindos Zone in the Hellenides, and represents an intermediate zone between the Internal and External Albanides. Most of the zone is filled with Cretaceous and Paleogene flysch formations and some limestone, but Triassic–Cretaceous limestone prevails in the Cukali Mountain (Mt.), with some outcropping of Triassic effusive rocks and Cretaceous-Eocene flysch formations. The *Kruja Zone* is analogous to the Dalmate Zone in the Dinarides and to the Gavrova Zone of the Hellenides. This zone consists of some elongated anticline structures of Cretaceous–Eocene carbonate cores of neritic limestone, dolomite limestone and dolomites covered by Oligocene flysch deposits. In the northern part of the zone, in the Tirana syncline, Tortonian molasse transgressively overlies flysch formations, while in the central part of the zone Burdigalian pre-molasse transgresses the flysch section. The carbonate section of the Kruja Zone plunges down to 10 km, where it is underlain by Triassic-Permian evaporate rocks (Velaj 1999, 2002; Frashëri 2007). The *Ionian Zone* extends in the southwestern part of Albania and continues as the Hellenides. Over Permian–Triassic evaporate rocks, the oldest rocks of this zone, there is a thick sequence of Mesozoic–Eocene carbonate rocks, mainly limestone and some dolomite limestone and chert. The carbonate rocks are covered by Oligocene and Neogene flysch deposits. They form three anticline belts dissected by longitudinal tectonic faults along their western flanks.

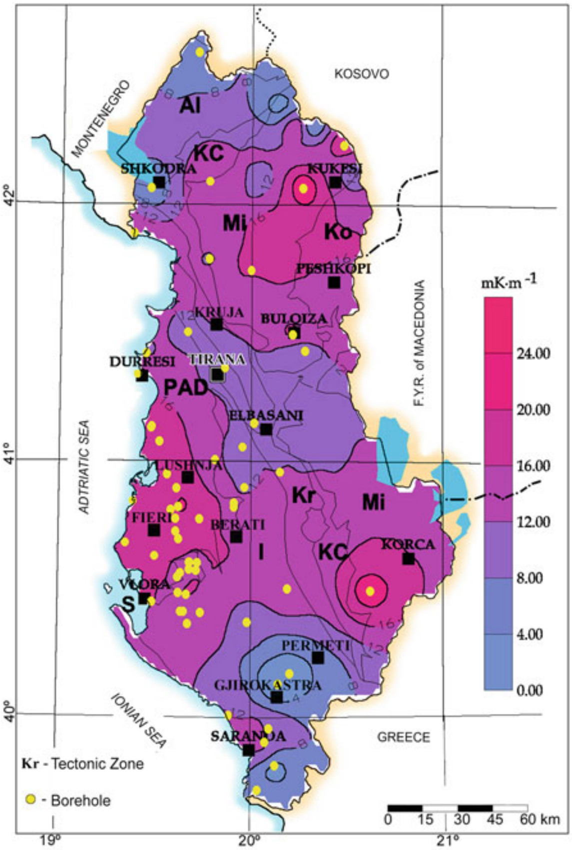
The *Sazani zone* is an integral part of the Apulia platform. A thick Cretaceous–Eocene limestone and dolomite section, transgressively covered by marly Burdigalian deposits, builds this zone. The *Peri-Adriatic Depression* (*PAD*) covers a considerable part of the Ionian, Sazani and Kruja tectonic zones. This is a foredeep depression filled with Middle Miocene to Pliocene–Quaternary molasse, whose thickness increases from the southeast to the northeast, reaching 5000 m near the Adriatic Sea. Molasse deposits usually lie transgressively over older ones, like the carbonate and flysch formation, and build a two-stage tectonic setting.

Geothermal Regime

Geothermal field studies and geothermal energy evaluations in Albania are based on temperature logs of 84 oil and gas wells and 59 shallow boreholes. The geothermal regime of the Albanides is governed by regional tectonics, lithological compositions, local thermal properties of the rocks, and the Earth's crust settings (Frashëri et al. 2004; Frashëri 2007).

The External Albanides, like the Dinarides, are characterized by a low geothermal gradient and the geothermal field features a relatively low temperature gradient (Fig. 2). The largest gradients are detected in the molasse anticline structures of PAD. The highest values of about 21.3 mK/m are observed in the

Fig. 2 Average geothermal gradient map of Albania (Frashëri et al. 2004)



Pliocene clay section (Frashëri et al. 2004, 2010; Frashëri 2007). Gradient decreases by about 10–29 % are observed in the carbonate anticline of structures in the Ionian Zone, where the gradient is mostly 15 mK/m. The lowest geothermal gradients, of 5 mK/m, are registered in the southern part of the Ionian Zone and in the Albanian Alps. Values of 7–11 mK/m are observed in a deep syncline belt of the Ionian and Kruja zones.

Modeling indicates that the gradient decreases at a depth of more than 20 km, which coincides with a crystalline basement top (Frashëri et al. 2004). Along the ophiolitic belt of the Mirdita Zone, geothermal gradients increase to 36 mK/m in the northeastern and southeastern parts of Albania (Fig. 2).

The maximal heat flow density of 42 mW/m^2 is observed in the center of PAD of the External Albanides. In the ophiolitic belt of the eastern part of Albania, heat flow density values are up to 60 mW/m^2. Increasing heat flow over the ophiolitic belt is linked with heat flow from granites of the crystal basement. There are some heat flow anomalies, which are conditioned by intensive heat transmission through deep faults.

Thermal Water Provinces

Albania's complex geological, structural and geomorphological conditions have resulted in the formation of heterogeneous aquifers with regard to their hydraulic type, resources, hydrodynamics and hydro-chemical characteristics (Eftimi 2010). Among them there are some deep aquifers related to different rocks like evaporate, carbonate and molasse, which host thermal waters. Most important data on thermal springs and deep wells are summarized in Tables 1 and 2.

Thermal waters of Albania are localized in four thermal water provinces: Korab, Kruja, PAD Basin and South Ionian Province; the main data on Albania's thermal waters, summarized in Tables 1 and 2 and a Piper diagram (Fig. 3), are used for an initial classification of Albania's thermal springs.

The *Korab Province* represents the central part of the Korab Zone, which is characterized by the presence of two tectonic windows (total surface area about 90 km^2), where gypsum dome structures outcrop (Melo et al. 1991). Deep circulating groundwater in gypsum forms two important sulfur thermo-mineral springs known as Peshkopia Spa, at the southwestern tectonic contact of the gypsum with surrounding Paleogene flysch formations (Fig. 3). The formation of the springs is related to a deep fault developed along the Black Drin River (Xhomo et al. 2002; Melo 1986; Melo et al. 1991). The water is of the SO_4–Ca-type, with elevated concentrations of Cl and HCO_3 and temperatures from about 35 to 43.5 °C. These waters feature low total dissolved solids (TDS), about 4 g/L, and H_2S of about 50 mg/L; the upward flow rate of the springs is about 23 l/s (Table 1). Shallow groundwater circulating in the gypsum deposits recharges a number of big cold sulfate springs (Fig. 4).

Calcium sulfate is formed by the dissolution of gypsum, according to the following reaction:

$$CaSO_4 \cdot 2H_2O \;\rightarrow\; Ca^{2+} + SO_4^{2-} + 2H_2O$$

If oxygen is absent and reducing conditions prevail, sulfate may be reduced by organic matter to produce hydrogen sulfide (Feng'e et al. 2005; Reimann and Birke 2010):

$$CaSO_4^{2-} + 2CH_2O \;\rightarrow\; CaCO_3 + H_2S + 2HCO_3^-$$

^-H_2S result to be an indicator for the bacterial activities which are more active at higher temperature (Andrejchuk and Klimchouk 2001; Feng'e et al. 2005).

Kruja Province overlaps a homonymous tectonic zone and is the most interesting province in terms of quantity and quality of thermal waters. The Tirana syncline, which represents the northern part of the province, comprises an artesian basin that features two important aquifers with thermal waters. Mesozoic-Paleogene

Table 1 Thermal springs of Albania; g–gypsum, l–limestone, d–dolomite; s–sandstone

Spring	Province, lithology	Q (l/s)	T (°C)	TDS (g/L)	Parameters (mg/L)									Chemical type
					H_2S	Ca	Mg	Na	Cl	SO_4	HCO_3	Br	J	
Peshkopi	Korab, g	23	43.5	4.0	50	826	100	279	488	1686	839	2.1	0.6	SO_4–Ca
Uji Bardhë	Kruja, l, d	20–100	22.5	6.0	350	389	168	1264	2382	616	532			Cl–Na–Ca
Llixha Elbasan	Kruja, l, d	16–28	55	6.8	403	794	199	1194	2359	1778	1000	5.5	1.1	Cl–SO_4–Na–Ca
Hidraj-Elbasan	Kruja, l, d	13–28	58	6.7	408	794	203	1150	2302	1753	447			Cl–SO_4–Na–Ca
Holta	Kruja, l, d	50–70	24.1	2.2		217	222	181[a]	245	1261	232			SO_4–Mg–Ca
Permet	Kruja, l	70–150	30	1.6	5.8	127	35	398[a]	702	157	212			Cl–Na–Ca
Leskovik	Kruja, l	15	26.7	1.0	7.0	103	30	205[a]	395	139	220			Cl–Na–Ca
Selenice	PBP, l		35.3	18.0	470	584	180	6045[a]	9936	364	832			Cl–Na
Karbunare	PBP, s	07–4.0	18.5	5.6	0.01	125	63	1258	1932	59.3	625			Cl–Na
Urra Vajgurore	PBP, l, d	500	17.5	0.5	14.0	69	11	98[a]	146	56	199			HCO_3–Cl–Ca–Na
Banjo Kapaj	Ionian, l, d	20	17.7	0.37		99	9.3	10.3	10.2	14.7	340			HCO_3–Ca

[a] The value is the sum of Na and K

Table 2 Deep wells with thermal water in Albania; g–gypsum, l–limestone, d–dolomite; s–sandstone

Well	Province	Depth(m)	Q (l/s)	T (°C)	TD (g/L)	Parameters (g/L)								Chemical type
						Ca	Mg	Na + K	Cl	SO_4	HCO_3	Br[a]	J[a]	
Dajç 2	Kruja, l, d	612	–	29.0	37.0	1.16	0.59	12.0	19.3	3.72	0.34			Cl–Na
Ishmi 1b	Kruja, l, d	2220	3.5	57.0	12.6	1.24	0.35	3.87	6.75	2.31	1.28			Cl–SO_4–Na–Ca
Shupal 1	Kruja, l,d	1794		29.5	2.37	0.27	0.13	0.32	0.36	1.28	0.6			SO_4–Cl–Ca–Mg
Kozan 8	Kruja, l, d	1837	10.3	65.5	4.1	0.64	0.14	0.73	1.43	1.51	0.24			Cl–SO4–Ca–Na
Galigat 2	Kruja, l, d	2914	0.9	45.0	5.67	0.7	0.12	1.21	2.20	0.94	1.00			Cl–SO_4–Na–Ca
Ardenica 12	PBP, s	3000	18.0	32.0	53.6	1.21	0.84	18.4	32.3	0.75	0.11	110	21.2	Cl–Na
Marinza 547	PBP, s			31.0	56.6	0.99	0.35	0.89	31.9	2.89	0.16			Cl–Na
Verbas 2	PBP, s	1035	1.3	29.3	8.2	0.32	0.28	31.2	4.60	0.03	0.56			Cl–Na
Seman 7	PBP, s	1980	30.0	67.0	20.7							25.0	30.0	Cl–Na
Grekan 4	Ionian, g	1214	0.7	35	326	1.40	2.90	120	191	7.2	1.9	768	0.84	Cl–Na
Delvina 4	Ionian, l	3780		21	69.0	4.60	1.20	20.8	38.3	1.92	3.78	114	35	Cl–Na

[a] Br and J are mesured in mg/L

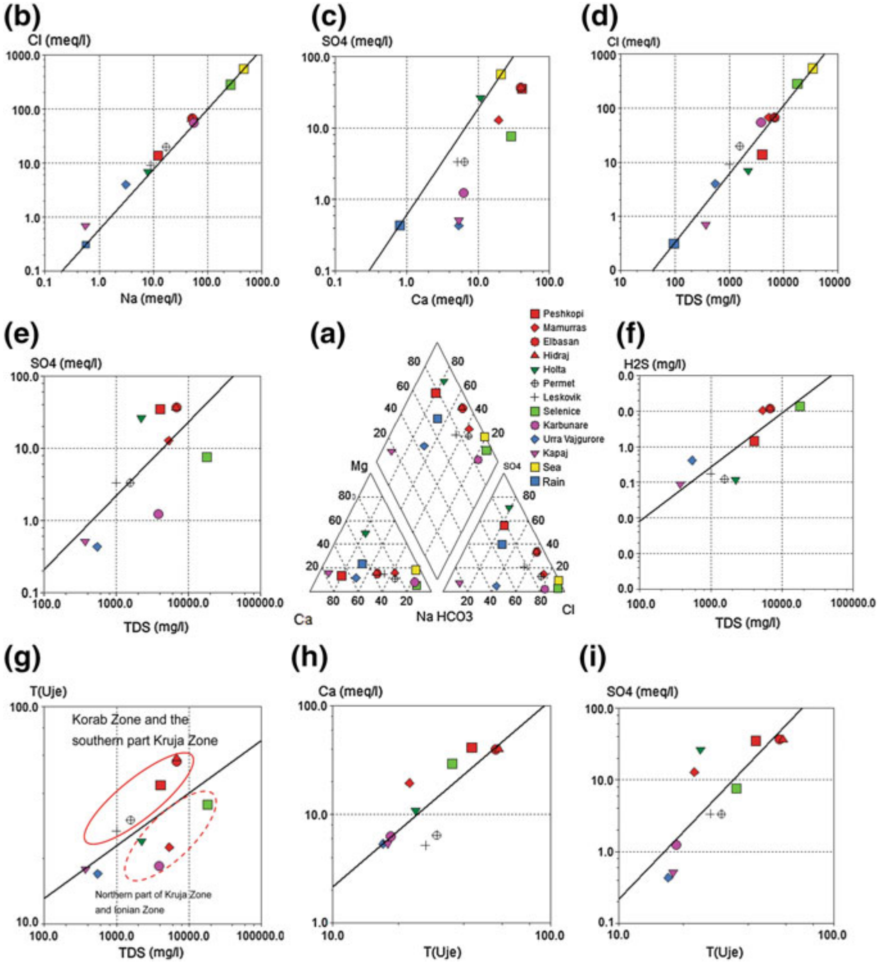


Fig. 3 Thermal springs: **a** Piper diagram. **b** Cl versus TDS. **c** SO_4 versus Ca. **d** Cl versus TDS. **e** SO_4 versus TDS. **f** H_2S versus TDS. **g** Temperature (T) versus TDS. **h** Ca versus T. **i** SO_4 versus T

carbonates, which host the first aquifer, form several outcrops and some deep buried anticline structures tectonically overthrown to the west. The second aquifer is represented by Neogene molasse rocks, mostly consisting of thick sandstone layers whose thickness increases to the northwest, to the Adriatic Sea (Fig. 5).

Albania's most important thermal springs are situated in Kruja Province, including Uji Bardhe near Mamuras, Llixha and Hidraj near Elbasan, and Holta, Permet and Leskoviku in southeastern Albania (Fig. 1).

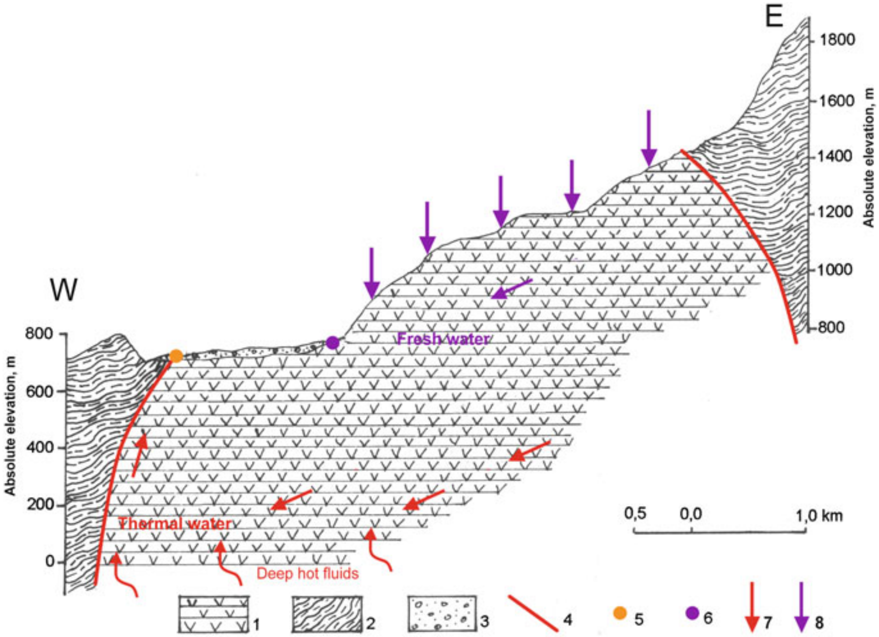


Fig. 4 Section through Peshkopia thermal spring: *1* Gypsum; *2* Flysch; *3* Alluvium; *4* Tectonic fault; *5* Peshkopi thermal spring; *6* Fresh water spring; *7* Thermal water flow; *8* Fresh water flow

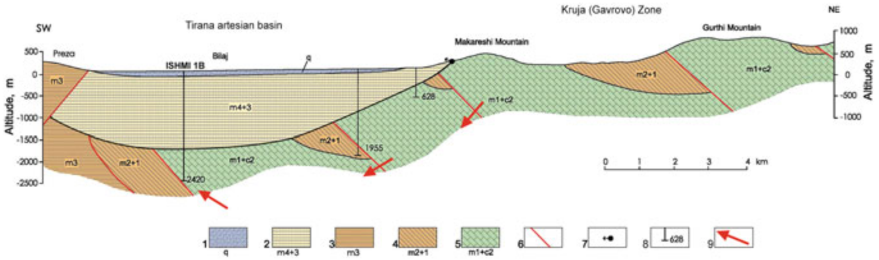


Fig. 5 Hydrogeological cross-section of the central part of the Tirana Basin: *1* Sands, gravels and silt; *2* Sandstones, siltstone and clays; *3* Clays, sandstones and siltstones; *4* Clays, siltstones and sandstones (flysch); *5* Limestones, dolomite limestones and dolomites; *6* Major fault; *7* Karst spring; *8* Deep artesian well and depth in meters; *9* Thermal water flow

Most of the springs emerge on the periphery of carbonate structures that recharge them, but Llixha and Hidraj springs rise along a supposed tectonic fault developed in Oligocene flysch formations (Fig. 6). The thermal water is formed in the Llixha anticline and moves upward along the tectonic fault developed in a Paleogene flysch formation over which an permeable olistolith horizon, about 20 m thick, facilitates ascending thermal water flow (Fig. 6).

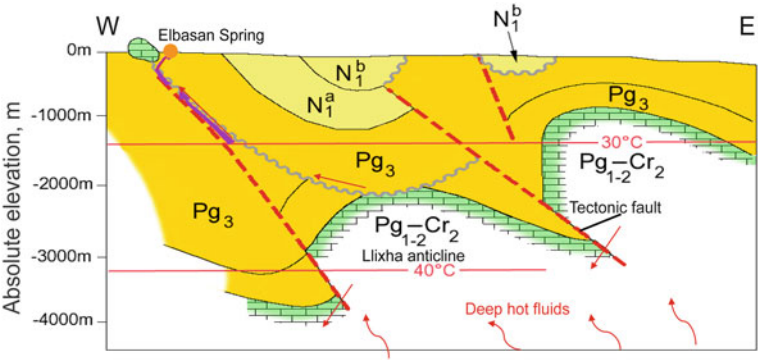


Fig. 6 Cross-section of the Llixha anticline

As shown in Table 1, the springs are quite different with regard to their physical and chemical characteristics but two hydrochemical types prevail: Cl–SO_4–Na–Ca and Cl–Na–Ca.

The Cl–SO_4–Na–Ca type comprises the thermal waters of the central area of Kruja Province, where the large springs of Mamurras, Elbasan (Llixha) and Hidraj emerge, as well as the deep wells Ishmi 1b, Kozan 1, Shupal 1 and Galigat 2 (Fig. 7). Their temperature varies from 22.5 to 65 °C the TDS is about 2.2–14.6 g/L. The waters are generally rich in H_2S, varying from 350 to 400 mg/L.

The maximal sulfide gas concentration of 1200 g/L is measured in the deep well Ishmi 1b. As the waters of this type are related to deep anticline structures, long groundwater circulation is assumed, which favors increases in Cl and Na concentrations. With regard to the enrichment of the waters with Ca and SO_4, it appears to be attributable to two processes; (a) ascending SO_4–Ca waters circulating in deep-seated evaporite deposits, and (b) pyrite oxidation according to the reaction (Appelo and Postma 1999; Reimann and Birke 2010):

$$2FeS + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$

Both processes are possible. The presence of evaporite rocks under the Mesozoic carbonate structure, backed by geological studies (Velaj 1995), facilitates sulfate hypogenic speleogenesis, allowing the transfer of hot water to springs. The second process is facilitated by the presence of pyrite crystals in the carbonate structures of Kruja Province (Eftimi 1998).

Thermal springs in the southernmost part of Kruja Province, specifically Permet and Leskovik, are of the Cl–Na–Ca-type (with elevated HCO_3 concentrations). They are characterized by low H_2S concentrations, varying from about 4 to 6 g/L. Temperatures vary from 26 to 31 °C. The groundwaters are fresh; TDS is about 1.0–1.6 g/L.

Fig. 7 Deep thermal water well Kozani-8 in Kruja Province

At some big springs of Kruja Province, like Mamurras and Permet, ascending thermal flows mix with shallow cold groundwater, resulting in significantly differing physical and chemical properties.

The molasse aquifer lies above the carbonate and flysch deposits and consists of an intercalation of sandstone, siltstone, and claystone deposits of Aquitanian to Serravallian age. As the active porosity of Neogene sandstone aquiferous rocks is generally low, the capacity of the wells is very small, usually less than 1.0 l/s (Eftimi 2003), and the temperature is generally lower than 25 °C down to a depth about 1000 m. A particular geothermal phenomenon of this province is the Postenan steam spring, issuing from a tectonic fault crossing the Postenan limestone anticline structure, but its characteristics have not yet been investigated.

Identified geothermal resources of Kruja Province, in carbonate reservoirs, are 5.9×10^8–5.1×10^9 GJ (Frashëri et al. 2004, 2007). Exploitable thermal water resources of Kruja Province could be increased, by drilling boreholes to tap thermal water structures at a suitable depth, which would mostly vary from about 500 to 1000 m.

The groundwaters of Kruja Province, particularly those of the well-known Llixha and Hidraj spas, but also of the deep wells Ishmi 1b and Kozan 2, are widely used in balneotherapy owing to their excellent curative properties.

Peri-Adriatic Basin Province (*PABP*) is a huge artesian basin, deepening to the NW under the Adriatic Sea. Three important aquifers have been identified in this basin: the deepest aquifer is that of carbonate rocks; the intermediate aquifer consists of sandstone Neogene molasse, and the upper aquifer is comprised of Pliocene sandstone–conglomerate formations.

The carbonate rock aquifer is tapped by deep wells located only on the southern periphery of the basin, mainly in the Patos–Verbas area. The highest water temperature of 50 °C is measured in well Bubullima 5, free flowing from the tapped depth interval of 2355–2425 m. Generally, the groundwater of this aquifer is highly mineralized and with a clear tendency to increase with depth, from about 1–3 g/L at depths around 1000 m to about 40–90 g/L at depths around 2000–2500 m. The water type is Cl–Na (Shtrepi 1971). With regard to gases, the presence of CH_4 and H_2S is evidenced but their concentrations have not been measured.

The Neogene molasse aquifer is tapped by deep wells located mostly in oil and gas fields. The total thickness of the Neogene molasse increases to the NW and along the Adriatic Sea coast it is about 5000 m. Thermal waters are localized mainly in Tortonian sediments, such as sandstone and conglomerates. Particularly significant are the free–flowing wells of Ardenica and Seman structures located in the central part of PABP (Table 2). The groundwater temperature of Ardenica wells varies from 32 to 38 °C and TDS from 38 to 56 g/L. In well Seman 3 (at the Adriatic Sea water line), the free-flowing groundwater temperature is 67 °C and according to calculations the temperature in the aquifer at a depth of 3758 m is around 100 °C. The chemical water type is Cl–Na and TDS is around 20 g/L. The thermal water tapped by the deep wells in PABP is rich in CH_4 gas, but the presence of H_2S has also been confirmed. Usually the water has a high content of Br and J, whose concentrations vary from 20 to 85 mg/L for Br and from 20 to more than 120 mg/L for J.

The formation of the Cl–Na-type thermal waters is related to groundwater metamorphism, due to long water-rock interaction mechanisms, and to the release of marine sedimentary water from the pores of the rocks in high pressure conditions.

The third PABP aquifer is related to the upper part of Pliocene deposits (Rrogozhina formation), with a maximal thickness about 750 m, consisting mostly of sandstone and conglomerate layers. The groundwater of the Rrogozhina formation is usually fresh to low mineralized, hard, with increased Fe concentrations and is of the HCO_3–Mg-type. Down to the maximal investigated depth of around 400 m, the water temperature is about 18 °C.

South Ionian Province is the largest thermal water province in Albania, but not the richest. This province consists of a number of Mesozoic carbonate anticline and syncline chains, filled mainly with Paleogene flysch formations, dipping to the NW, under the Peri-Adriatic Basin. The presence of thermal springs has not been identified in this province; there are only big fresh water springs and springs like Banjo Kapaj whose is temperature is 17.5 °C. Some deep oil and gas wells located in the northernmost part of the province discharge free-flowing, high temperature and highly mineralized groundwater. Among them the most important is well

Grekan-4, situated in the eastern periphery of the Dumre gypsum dome. This well spurts groundwater from a depth of about 1200 m; the groundwater temperature is 35 °C, TDS about 325 g/L, and bromine concentration about 768 mg/L. Some deep wells drilled in the Delvina syncline, in South Albania, also discharge highly-mineralized groundwater of the Cl–Na-type.

Geothermometry

According to the results reported in geothermal studies of Albania, the temperature at a depth of 500 m is between 21 and 24 °C. The highest temperatures, up to 36 °C at 1000 m and 105.8 °C at 6000 m, have been measured in some deep PADP boreholes. The same temperatures have also been recorded in some boreholes in the ophiolitic belt. The lowest temperatures were measured in the mountainous regions of the Mirdita Zone, as well as in the Albanian Alps, where there is intensive circulation of cold karstic descending water whose temperature is less than 8 °C. The same occurs around huge karst massifs in South Albania, where zero gradients are measured in some deep boreholes, like Kalcat, which is about 2000 m deep (Frashëri et al. 2004).

Geothermometers are used to provide an indication of temperatures in geothermal reservoirs. It is a known fact that geothermometers measure different aquifer temperatures at same sampling points (Kharaka et al. 1989). This is supported by the results of aquifer temperature calculations for some thermal springs of Albania (Table 3). The mean estimated temperatures of all thermal springs, as calculated by Na, K and Ca geothermometers, are similar and vary between 197 and 230 °C. Based on geothermal modeling, one can suppose that thermal waters rise from depths of about 8-10 km, with temperatures as high as 220 °C (Frashëri et al. 2004).

Table 3 Temperatures of thermal springs calculated by means of geothermometers

Thermometer	References	Thermal springs				
		Peshkopi	Mamurras	Llixha Elbasan	Hidraj	Mean for all springs
Na/K	Fournier (1973)	273	180	236	231	230
Na/K	Trusdell (1975)	269	184	236	231	230
Na–K–Ca	Fournier (1979)	191	188	206	203	197
Na/K	Fournier (1979)	279	214	254	251	249
Na/K	Fournier and Potter (1979)	308	234	279	275	274
N–K–Ca with Mg	Fournier (1979)	108	36	68	65	69.0
K/Mg	Giggenbach (1988)	48	45	43	44	45

Conclusions

The geothermal regime of the Albanides is governed by regional tectonics, lithological compositions, local thermal properties of the rocks, and the Earth's crust settings. Albania in general is characterized by low geothermal gradients. The main hydrogeological and hydrochemical characteristics of the thermal waters of Albania are presented in the paper. Four thermal water provinces, with well-defined chemical characteristics, are distinguished. Geological–structural, thermal and hydrochemical characteristics are described for each province.

Korab Province is characterized by the presence of H_2S thermal waters of the SO_4–Ca type, whose temperature is 43 °C. Kruja Province is the richest in thermal waters of the Cl–SO_4–Na–Ca and Cl–Na–Ca-types; H_2S concentrations are usually greater than 250 mg/L. Most PADP thermal waters are highly mineralized, of the Na–Cl type, with CH_4 and H_2S gases, and usually with high Br and J concentrations. South Ionian Province is the poorest in thermal water, but near the Dumre gypsum dome high–temperature Cl–Na thermal water with a bromine content of about 768 mg/L is tapped at a depth 1200 m.

The highest measured thermal water temperature in Albania is 83 °C, but the aquifer temperature calculated by means of geothermometers is greater than 200 °C.

Albania's thermal water resources are used by some health spas, like the well-known spas of Peshkopi, Elbasan, Hidraj and Bilaj. Their exploitable resources could be increased by drilling boreholes.

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Geothermal Potential of Macedonia and Its Utilization

S. Popovska-Vasilevska and S. Armenski

Abstract Macedonia is characterized by low-temperature geothermal energy utilization; the medium and high-temperature potential is still unexplored. Nevertheless, even currently available resources are under utilized by far. The majority of exploited thermal waters in Macedonia are used mainly by agricultural consumers and thermal spas. Macedonia has a rich and long experience in geothermal energy use, with a wide range of application possibilities, reliable exploitation, and economy of use, despite the relatively obsolete technologies applied. When compared to other renewable energy sources, geothermal energy offers the highest reliability of supply and the lowest price of energy. Taking into account the state of the country's economy, for three decades there has been no significant progress in the field of geothermal energy. Except for rare cases of reconstruction and optimization of existing projects, the general picture is even worse than before.

Keywords Thermal waters · Geothermal potential · Macedonia

Introduction

The use of thermal waters in today's Macedonia has been traditional since before Christ, as evidenced by discovered ruins of old Roman baths and coins. More "recently", the tradition became more pronounced during the Ottoman occupation, which lasted for five centuries and brought a "new culture" of human hygiene, health and relaxation.

S. Popovska-Vasilevska (✉)
University St. Kliment Ohridski, Makedonska falanga 33, 7000 Bitola, Macedonia
e-mail: sanja.popovska-vasilevska@tfb.edu.mk

S. Armenski
Ss. Cyril and Methodius University, Karpos II, bb., 1000 Skopje, Macedonia
e-mail: armen@mf.edu.mk

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In the 1970s and 1980s, the Republic of Macedonia was one of the promoters of direct application of geothermal energy, particularly in agriculture. Unfortunately, this period of progress in geothermal energy development ended in the early 1990s due to the country's economic and political transformation. However, the interest in this resource is slowly coming back, as a consequence of the global and national energy and environmental situation.

Macedonia is situated in the central part of the Balkan Peninsula, along a very favorable geothermal zone that starts in Hungary in the north and Italy in the west and stretches through Greece down to Turkey and beyond to the East. Existing natural springs and exploration data indicate that it is the one of the richest countries in low-enthalpy geothermal energy resources, and this is due to a diverse geological composition and continual tectonic processes in the past. Four main tectonic units have been identified: Serbian–Macedonian Massif, Vardarian Zone, Pelagonian Massif, and West Macedonian Zone (Fig. 1), each with a completely different composition and evolution of the relief. Thermo-mineral waters with different physical and chemical characteristics emerge above rift lines between them. Known geothermal fields are grouped according to Macedonia's geotectonic divisions. The east and northeast, as part of the Serbian–Macedonian Massif, is characterized by crystalline basement rocks and are much richer than the west and southwest (Bosnian–Serbian–Macedonian geothermal area), characterized by limestone (Popovska-Vasilevska and Armenski 2015).

There are seven main geothermal fields (Fig. 1) in Macedonia with 18 thermal water localities, including more than 50 occurrences as springs and wells. Most geothermal occurrences in Macedonia are connected with the Vardar tectonic unit (Fig. 1). Only a few occurrences (Debarska Banja and Kosovrasti) are situated away from this unit and its contacts (Popovska-Vasilevska and Armenski 2015).

Most of the thermal waters can be found up to an altitude of 400 m above sea level. Only the Kozuv Mountain springs and Banjiste wells are at an altitude of 600 m.

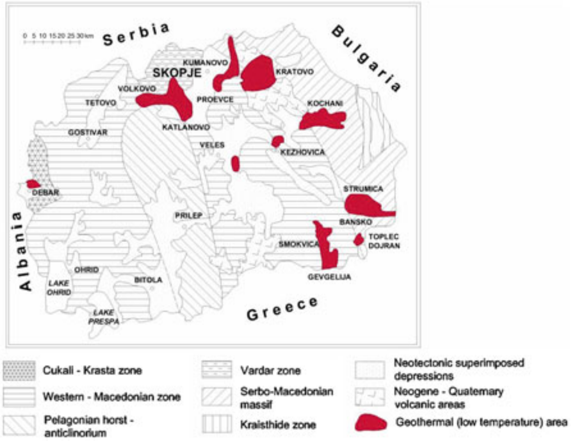

Fig. 1 Main geothermal areas in Macedonia and regional tectonic setting (Arsovski 1979)

Traditionally, thermal waters in Macedonia are associated with thermal spas, and in the more recent history with greenhouse heating as well. As Macedonia's typical geothermal resources feature low temperatures, the main uses of the energy and chemical composition include: greenhouse heating, space heating of a small number of public buildings and hotels, CO_2 extraction, industrial applications in the past, and balneotherapy. According to the Energy Balance of the Republic of Macedonia for the period 2015–2019, in 2014 geothermal energy contributed 269 TJ to the primary and final energy consumption, or represented 0.244 and 0.36 %, respectively, of the primary and final energy consumption. In the energy balance of renewable energy sources for the same year, geothermal energy participated with 2.36 % (Official Gazette of the Republic of Macedonia 2015–2019). There is still no power generation from geothermal energy, but there are indications of foreign interest to explore and utilize the potential.

Known Thermal Water Resources in Macedonia

Out of the seven geothermal fields identified in the eastern and northeastern parts of the country, four have been found to be very promising and three have been investigated to a level where practical use is possible. Except for the springs in Debarska banja and Kosovrasti, which are situated in the Western Bosnian–Serbian–Macedonian geothermal zone, all other springs are located in the Central Serbian–Macedonian Geothermal Massif, Central and Eastern Macedonia (Popovska-Vasilevska and Armenski 2015).

The total available flow of exploitable resources is 922 l/s, where the maximal measured short-lasting flows are 1397 l/s (Popovski et al. 2010).

Thermal water temperatures vary in the range from 24–27 °C (Gornicet, Volkovo and Rzanovo) to 70–78 °C (Bansko and Dolni Podlog) and the average temperature is 60 °C (Popovska-Vasilevska and Armenski 2015).

The biggest potential exists in the Kocani geothermal field, with a total maximal flow of up to 350 l/s and temperatures of 65 °C (Istibanja) and 75–78 °C (Dolni Podlog). Next is the Gevgelija geothermal field, with about 200 l/s and temperatures of 50 °C (Negorci) and 65 °C (Smokvica). Others include: Debar geothermal field with 160 l/s and temperatures of 40 °C (Debarska banja) and 48 °C (Kosovrasti), Strumica geothermal field with 50 l/s and 70 °C, and Kratovo/Kumanovo geothermal field with 71 l/s and temperatures of 31 °C (Kumanovska banja) and 48 °C (Kratovo) (Popovska-Vasilevska and Armenski 2015).

Macedonian thermal waters belong to the group of low-temperature geothermal resources. So far, thermal water uses in Macedonia include thermal spas, greenhouse heating, drying of agricultural products, district heating, and preparation of sanitary warm water. Power generation is still not practicable, given that the maximal available temperatures (76–78 °C) are below the limit of technical feasibility for application.

Currently, the generally accepted effluent temperature of 20 °C is the lower limit for use, but it has already been proven that 15 °C could be achieved in practice (cold fish farming, heat pumps, etc.). Table 1 shows simulated values, according to different outlet temperatures, for all exploitable geothermal resources in Macedonia. A total available maximal heat power of 173 MW could be obtained, which suggests the possibility of a maximum annual output of 1.5 TWh. This is only a theoretical indication considering that each project has a different exploitable temperature difference range, annual utilization factor and type of application.

Thermal Resources in Use

About 15 geothermal projects have been implemented in Macedonia in the 1970s and 1980s (Table 2). Some of them are still in service but others have been abandoned or operate below design capacity. Four of them are very important and have a major influence on the development and application of geothermal energy in the country. These are the Kocani geothermal project, the Smokvica and Istibanja agricultural geothermal projects, and an integrated project in Bansko (Popovski et al. 2010).

Kocani Geothermal Project

The project is located in the region of Kocani Valley, where 18 ha of greenhouses are heated since 1982 and there is also a rice drying plant (not in operation) (Table 3). Non-corrosive water enabled a simple technical design (direct use of brine in user heating systems). A subsequent successfully drilled well, which increased the flow rate from 300 to 450 l/s, opened the way for the introduction of geothermal energy utilization in other sectors as well.

The geothermal project "Mosha Pijade" is located near (only about 100 m from) the geothermal production wells at Podlog, in the Kocani geothermal field. It consists of a 6 ha (4·1.5 ha blocks) greenhouse complex, heated solely by geothermal energy.

The Kocani geothermal project either the single one which continuously operates from the beginning, it suffers many problems. One of the most serious issues is the need to ensure a reasonable annual heat loading factor of the integrated system, in order to achieve technical and economic viability. Deployment of installed heat power is very irregular on an annual basis, i.e. the system is engaged at maximum power for only three months, in the heating season (winter). Such an approach leads to unsustainable resource and system utilization.

Table 1 Energy estimation of geothermal resources in Macedonia for different effluent temperatures (Popovski et al. 2010)

Geothermal field		Flow	T	Theoretically available heat capacity for different temperatures of the effluent thermal water (MW_{th})						
		l/s	°C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C
01	Dolni Podlog-Kochani	300	75	75.4	69.1	62.8	56.5	50.2	44.0	37.7
02	Istibanja-Vinica	73	65	15.3	13.8	12.2	10.7	9.2	7.6	6.1
03	Kratovo geother-mal field-Kratovo	20	48	2.8	2.4	1.9	1.5	1.1	0.7	0.3
04	Strnovec-Kumanovo	46.71	40	4.9	3.9	2.9	1.9	1.0	–	–
05	Kumanovo spa-Kumanovo	4	31	0.3	0.2	0.1	–	–	–	–
06	Dobrevo-Zletovo	8	28	0.4	0.3	0.1	–	–	–	–
07	Bansko-Strumica	50	70	11.5	10.5	9.4	8.4	7.3	6.3	5.2
08	Smokvica Gevgelija	120	65	25.1	22.6	20.1	17.6	15.1	12.6	10.0
09	Negorska spa-Gevgelija	80	50	11.7	10.1	8.4	6.7	5.0	3.4	1.7
10	Kezovica-Shtip	20	60	3.8	3.4	2.9	2.5	2.1	1.4	1.3
11	Raklesh-Radovish	1	26	0.1	–	–	–	–	–	–
12	Topli dol and Mre-zichko-Rzanovo	2	27	0.1	–	–	–	–	–	–
13	Katlanovo-Skopje	13	50	1.9	1.6	1.4	1.1	0.8	0.5	0.2
14	Volkovo Skopje	20	25	0.8	0.4	–	–	–	–	–
15	Gornichet	5	24	–	–	–	–	–	–	–
16	Debarska spa-Debar	100	40	10.5	8.4	6.3	4.2	2.1	–	–
17	Kosovrasti-Debar	60	48	8.3	7.0	5.8	4.5	3.3	2.0	0.7
18	Kosel-Ohrid	–	–	–	–	–	–	–	–	–
	Total	922.4		172.9	153.7	134.3	115.6	97.2	78.8	68.2

Table 2 Geothermal projects in Macedonia (Popovski et al. 2010)

Geothermal location	Geothermal field	Application	Heat power		Heating installation
			Total kW	Geoth. kW	
Istibanja	Kocani	Greenhouse heating (6 ha)	17.500	12.350	Aerial steel pipes (reconstruction of the existing installation with heavy oil boiler)
Bansko (integrated geothermal project)	Strumica	Greenhouse heating (2.9 ha)	9.000	9.000	Aerial steel pipes and on the soil surface steel pipes.
		Greenhouse heating (600 m^2)	150	150	Corrugated PP pipes on soil surface + fan jet air heating
		Plastic houses heating (3 ha)	3.000	3.000	Soil heating
		Space heating	1.560	1.560	Aluminum radiators
		Sanitary warm water preparation	700	700	Plate heat exchangers + warm water accumulator
		Swimming pool heating	350	350	Plate heat exchanger
Podlog	Kocani	Greenhouse heating (6 ha)	17.500	17.500	Aerial steel pipes
Kocani (District Heating scheme)	Kocani	Greenhouse heating (12 ha)	40.700	20.500	Aerial steel pipes.
		Rice drying	1.600	1.600	Square finned pipes heat exchanger (water/air)
		Paper industry	3.200	3.200	Plate heat exchanger
		Space heating	650	650	Aluminum and iron radiators
Smokvica	Gevgelija	Greenhouse heating (22.5 ha)	65.500	11.750	Aerial steel pipes + corrugated PP pipes on soil surface)
		Plastic houses heating (10 ha)	10.000	10.000	Corrugated PP pipes on the soil surface

(continued)

Table 2 (continued)

Geothermal location	Geothermal field	Application	Heat power		Heating installation
			Total kW	Geoth. kW	
Negorci	Gevgelija	Space heating Balneology	250	250	Steel radiators
Katlanovo	Skopje	Balneology			
Kumanovo	Kumanovo	Balneology			
Banja	Kocani	Balneology			
Kezovica	Stip	Balneology			
Kosovrasti	Debar	Balneology			
Banjishte	Debar	Balneology			

Table 3 Summary information on Kocani's existing plants (Popovski et al. 2010)

	Connection			Geothermal energy user			
User	∅	Distance	Water flow	Heating system	Temp. regime	Heat power	Average annual heat gain
	mm	m	l/s		°C	MW	GWh
12 ha green-house complex Kocansko pole-Kocani	300	3.000	100–150	Aerial steel pipe heating	75/35	20.50	21
6 ha greenhouse complex Mosha Pijade-D. Podlog	257	150	60	Aerial steel pipe heating	75/35	17.50	16
Rice drying unit (not in operation)	109		13	Copper pipes	75/50	1.36	0.8
Joint distribution pipeline for the industry and district heating	406–324	7.000	190–250	Different heating systems	75/30	39.8–52.3	59.4 (final 99/100)

Istibanja Geothermal Project

Vinica is situated at 10 km from Kocani, where the second geothermal system Istibanja of the Kocani geothermal field is located.

The greenhouse complex in Istibanja uses geothermal energy from a neighboring system of wells and consists of 8 “Venlo” blocks (1.5 ha each, total = 12 ha). The system has not been completed and was never fully operational. In fact, the makeover of equipment to enable the use of thermal water as the heating fluid suffered from lackluster design and installations. Some important adjustments appear to be necessary, such as installation of additional heating pipes and a thermal water storage system, and other reconstructions. In-depth studies and efforts are needed to properly complete this geothermal system.

Bansko Geothermal Project

At present, the system services the users listed under points 1, 2 and 5 in Table 4. Other potential users (or those still unconnected) are listed under points 3, 4, 6, 7.

The existing heat users, those not yet connected, and potential users could together reach a total installed power of 22 MW. That is far more than the existing 10.3 MW, which is the theoretically available potential if the effluent water temperature can be limited to 25 °C. Presently, the exploited heat power is only about 8 MW because effluent water is maintained by many users at up to 40 °C and very short-time peak loads are also covered by geothermal energy, which leads to over-exploitation and depletion of the resource.

A recently proposed configuration comprises geothermal heat use in cascades, which would ensure a much better annual heat loading factor. This is possible due to the wide range and different kinds of applications. If the maximal allowable flow from well B1 is 52 l/s, it should be possible to reach an annual heat loading factor of about 0.4, which is a very high value for the considered heat users and local climate conditions, and would enable a very competitive price of the supplied heat energy.

Smokvica Geothermal Project

The greenhouse complex “Gradina”, which is a rather large heat consumer, consists of 22.5 ha of glass and 10 ha of plastic greenhouses. The installed power of the heating system is about 75 MW and the annual heat consumption about 80 GWh/season (depending on the selected crops and external climate conditions). This corresponds to 8000 t/year (initial variant) of heavy fuel oil, i.e. 2,400,000 US $/year for a total commercial value of the produce of about 3,500,000 US$/year (68 % share).

Both the connection line, about 6 km long, and the greenhouse heating systems have been designed to use thermal water directly, i.e. the previous “soft” water in the closed-loop heating system has just been replaced with thermal water in an open-loop system. In addition, the thermal water needs to be heated to higher temperatures in the boilers when the load exceeds the heat power of the geothermal

Table 4 Heat users of the "Bansko" integrated geo-project (Popovski et al. 2010)

No.	User	Maximal heat power		Maximal heat power of geothermal origin		Necessary geothermal water flow
		MW	°C	MW	°C	l/s
1	Zik Strumica					
	• Greenhouse complex	3.98	70/40	3.98	70/40	31.72
2	Hotel "Car Samuil"					
	• Heating rooms	1.56	80/40	0.80	70/40	6.37
	• Sanitary warm water	0.50	50/38	0.50	70/25	2.65
	• Swimming pool	0.15	40/25	0.15	40/25	2.39
	• Medical recreation		38			
3	Hotel ZIK "Spiro Zakov"					
	• Heating rooms	0.38	80/40	0.20	70/40	1.59
	• Sanitary warm water	0.22	50/40	0.22	70/25	1.17
4	Hotel ZIK "Strumica"					
	• Heating rooms	0.20	80/40	0.12	70/40	0.96
	• Sanitary warm water	0.12	50/40	0.12	70/25	0.64
5	Private farmers					
	• Complex Of Small Soft Plastic Covered Greenhouses	1.00	40/25	1.00	40/25	15.93
6	Open air swimming pool					
	• Sanitary warm water	0.06	40/25	0.06	40/25	0.96
	• Swimming pool	0.15	40/25	0.15	40/25	2.39
7	Rest house for children and retired people					
	• Heating rooms	0.45	80/40	0.25	70/40	1.99
	• Sanitary warm water	0.25	50/40	0.25	70/25	1.33
	Total	9.02		7.80		70.09

energy source. Since thermal water is aggressive, because it contains free O_2 and CO_2, such a solution during the first year of use resulted in complete destruction of the heating installations in the greenhouses and fire pipes in the boilers. The connection pipeline was damaged in several places as well.

As a consequence, major problems were encountered with the operation of the Gradina geothermal system in Gevgelia. The economic effects of the introduction of the "free of charge" energy source have been minimal.

Active reconstruction was initiated in 1988. The first phase was completed by 1991 and yielded the expected positive results. However, the owners had neither capital nor organizational capability to finalize the reconstruction, such that the results achieved were only temporary. This project is very important for other geothermal projects in Macedonia because if such a "problematic" project can be profitable, then it would be much easier to find feasible solutions for other projects.

Other Projects

Other projects in Macedonia are mainly associated with recreational uses, except in the Katlanovo, Negorci and Debarska spas, where geothermal water is used for space heating too.

Thermal Spas in Macedonia

The use of thermal waters for medicinal purposes has been known since ancient Greek and Roman times. Particularly the Romans used to build luxury baths for public and private use. Following a decline in the Middle Ages, thermal waters became very popular once again during the long Turkish occupation and there were numerous public and private baths. After World War I, a more systematic approach to the problem was followed (chemical analyses, medical research, etc.); however, no modern spa centers were built. The seven existing spas date back to the period between 1960 and 1980. After 2005, there were some initiatives and interest in recovery and upgrading.

The temperatures of the thermal waters used for balneotherapy differ, depending on the location and the geothermal field in question. The highest water temperature is recorded in Bansko Spa (73 °C), followed by Banja–Kocani (55 °C), Kezovica Spa (54 °C), Katlanovo Spa (40.5 °C), Debar Spa (38.6 °C), Negorci Spa (38 °C), Kumanovo Spa (31 °C), etc. The order of available flow rates is the same, i.e.: Debar Spa (91.2 l/s), Kosovrasti Spa (68.8 l/s), Bansko Spa (35 l/s), Kumanovo Spa (3,34 l/s), Kezovica Spa (5.4 l/s), Negorci Spa (1.8 l/s), etc. (Georgieva and Popovski 2000).

From a chemical point of view, thermal flows can be divided into two groups: acidic thermo-mineral waters and sulfuric, iodic, radioactive, fluoric waters. The most prevalent are acidic waters with TDS levels of 500–5000 mg/l, and the majority feature excellent curative properties. The radioactivity of some of these waters is significant, as in the case of Kezovica Spa (588 Bq/l), Kosovrasti Spa (455 Bq/l), Banja–Kocani Spa (360 Bq/l), etc. (Georgieva and Popovski 2000).

The curative properties of the spas are largely associated with the chemical composition of the thermal water and specific local climate conditions.

Debar Spa is located 4 km away from the town of Debar, near the Albanian border, at 780 m above sea level, below the Krcin and Deshat mountains. The climate is moderate but can be quite cold during the winter months. Thermal waters are of the sulfur and iron types, depending on the source in question. The sulfuric thermal waters are used for curing rheumatism, sciatica, eczema and female illnesses, while the iron water is used for drinking and bathing to cure gastric, kidney and urinary ailments, bronchial asthma, diabetes, gout, and anemia. Debar Spa is among the oldest spas in Macedonia (about 700 years old).

Katlanovo Spa is the oldest and best known spa in the country, dating back to the ancient Greek times. In the Roman times it was a very important regional medical center. The spa is located 15 km from Skopje (capital of Macedonia), near the highway to Greece and in an isolated mountainous location, with clean air and a calm atmosphere. Several springs produce thermal waters of the sulfur-iodine type but also of the alkaline-carbon–acid type. The sulfur-iodine waters are used for bathing, to alleviate rheumatism, paralysis, neuralgia, female illnesses, diabetes and the consequences of injuries. Hot alkaline waters and carbon/acid waters are used to address health problems associated with blood circulation, stomach ailments, high blood pressure etc. Cold alkaline and radioactive waters are used against stomach and urinary conditions.

Banja Spa is 6 km from the town of Kocani and has also been known since the Roman times. The thermal water is of the sulfur type, with low TDS and radioactivity. It is used for curative purposes against rheumatic, skin and female ailments, inflammation of joints, muscles and veins, and stomach, gall bladder and urinary conditions.

Kosovrasti Spa is near the town of Debar, near the Albanian border. It is very near Lake Debar, at an altitude of 550 m. The spa is about 700 years old, like Debar Spa. It was very famous during the Turkish times, when it was beautifully outfitted and landscaped. The thermal waters are highly sulfurized but also contain carbonates. Some of them are highly radioactive. They are curative against sciatica, rheumatism, female ailments and other conditions.

Kumanovo Spa is about 3 km away from the town of Kumanovo, near the railway line to Belgrade. The mineral water is of the calcium–magnesium–iron-type and used to alleviate stomach, kidney, liver and urinary ailments and high blood pressure. It is located in beautiful surroundings with many recreational features.

Negorci Spa is located in the far south of Macedonia, near the town of Gevgelija. The climate is typically Mediterranean. The water is used to cure rheumatism, sciatica, neuralgia, paralysis, female ailments and skin conditions. This spa has a long history; it was developed in 1903 by the local Turkish pasha and improved upon after World War II.

Bansko Spa is located below the mountain of Belasica, in the village of Bansko. This spa, known in ancient Greek and Roman times, was later abandoned. Then, 300 years ago it was rehabilitated by the Turks and has been in continuous use since then. The largest health center is the Tsar Samuil Hotel but there are also several small hotels and guest houses. The thermal water is the hottest one in Macedonia (75 °C) and is of the iron-sulfuric type. It is used to alleviate rheumatism and sciatica.

Kezovica Spa is located in a suburb of the town of Shtip in East Macedonia. It is long known but there are no actual records. The thermal water is of the chloride–hydrocarbonate type, quite radioactive (588 Bq/l) and measures a high temperature

(66 °C). It is used to alleviate rheumatism, joint inflammations, female ailments, some skin conditions, etc. (Georgieva and Popovski 2000).

There are also another 19 thermo-mineral springs in the country, suitable for balneotherapy. So far there is no relevant information about their potential activation.

The temperatures and flow rates of the thermal waters in Macedonia's spa centers, at least those of the known springs and wells, allow energy uses at only some of them, i.e. in Bansko, Negorci, Katlanovo and Debar and Kosovrasti. At present, the following uses and activities are known:

- At Bansko Spa, the water is used to heat a greenhouse complex of 3.2 ha, the Tsar Samuil Hotel, and a number of small plastic greenhouses. It is also used for the preparation of sanitary warm water for hotels in the village and a recreational swimming pool at the Tsar Samuil Hotel. The use of geothermal energy for heating, as a substitute for heavy fuel oil, saves more than 300,000 US$/year.
- At Negorci Spa, the entire spa complex is heated by thermal water and a warm sanitary water supply provided. This results in savings of more than 100,000 US $/year.
- At Katlanovo Spa, substitution of heavy fuel oil by geothermal heat probably saves in excess of 200,000 US$/year.

With regard to the other spas, it is difficult to expect any serious engagement before resolving the problem of needed investment in reconstruction of the buildings and infrastructure, after many years of improper maintenance. In any case, Debar Spa and Kosovrasti Spa have temperatures and flows of geothermal water that enable the implementation of significant energy projects.

Overall, it can be concluded that:

- The Republic of Macedonia is rich in geothermal resources, which offer opportunities for the generation of large-scale health spa business. However, there are only eight spas at present and no development efforts are under way.
- The condition of the existing spas is poor due to the country's economic circumstances. All of them require major reconstruction and renovation. Investors in such activities cannot be found in the country, so the only possibility is foreign investment.
- Current use of the spas for medical treatment only cannot guarantee their future. Poor social insurance cannot cover the operating expenses of the spa centers. Much higher contributions from guests coming as ordinary tourists should be sought.
- The above can be achieved only by introducing new offerings, which would make the spas attractive not only to convalescents, but also to ordinary families and young people.
- Expanding current recreational offerings by adding fitness facilities and out-of-season training centers for athletes is a highly prospective possibility.

- At conveniently located spas (Katlanovo Spa, Bansko and Negorci Spa), the addition of aqua parks could be a realistic long-term solution for profitable business.

Studies indicate excellent economic viability based on the existing market fordomestic and foreign guests (Georgieva and Popovski 2000).

Overview of Other Unexplored and Unexploited Geothermal Resources

The most significant convective geothermal systems in Macedonia are: Skopje Valley, Kocani Valley, Strumica Valley, Gevgelija Valley, Kezovica, Toplik–Topli Dol on Mt. Kozuv, Toplec near Dojran, Proevci near Kumanovo, Strnovec, Zdravevci on the Povishnica River near Kratovo, Sabotna Voda near Veles, and systems in the western part of Macedonia–Kosovrashka Banja, Debarska Banja, and Banishe on the Pena River near Tetovo. The quantity of geothermal energy in the hydro-geothermal systems can be determined applying different geothermal potential assessment methodologies. All of them address a number of hydrogeological, geological and geothermal parameters, determined (or approximated) in advance. The more reliable the parameters are known, the better the approximation. The estimates provided below are based on a volumetric methodology.

The following input values were used to calculate the quantity of the geothermal energy contained in geothermal systems: average temperatures of the rocks and the fluid in the reservoirs, average effective porosity of the rocks in the reservoirs, average specific heat of the rocks, surface and thickness of the reservoirs, temperature in the "neutral" layer, average specific heat of the thermal waters in the reservoirs, and average density of the waters. The extent of reservoirs (i.e. surface and thickness) was taken from data collected in previous measurements and analyses. The temperatures in question were taken from measurements in conductive systems and from chemical geothermometers in convective ones. Other data came from standard tables and results of engineering/geological investigations of rocks in Macedonia (Popovski and Lund 1999).

The resulting predictions of temperatures and geothermal energy reserves in Macedonia's geothermal fields, which remain unexplored and unexploited, are shown in Tables 5, 6 and 7. The calculation method for geothermal energy reserves was volumetric, with a stochastic approach. Predicted reserves are shown separately for conductive and convective hydro geothermal systems. The calculation of reserves was based on the maximal approach, with a potential utilization factor (Rg) of 10 %. The maximal reserves were calculated as heat energy accumulated in the rocks and thermal waters in the reservoir.

According to previous local and worldwide experiences, it is possible to develop the reserves into productive energy sources. In practical terms, it is possible to develop most of the reservoirs into exploitable energy sources, with

Table 5 Predicted temperatures of systems with active occurrences of hot water (spring or borehole) in Macedonia (Popovski and Lund 1999)

No.	Locality	Appearance	Prognosis temperature (°C)
1	Volkovo	GTD–1/76	80–90
2		D-1/75	80–90
3	Katlanovo	B-1	80–115
4		Nervna voda	80–115
5		D-1/78	80–115
6		Spring	80–115
7	Sabota voda	Borehole	80–100
8	Podlog	IBMP	100
9	Banja	B/1	100
10	Istibanja	I-5	100
11	Bansko	Borehole	115–120
12	Ldji		100–115
13	Kezovica	Borehole	100–115
14	Smokvica	Borehole	70
15	Negorci	Borehole	75–100
16		Borehole	75–100

Table 6 Predicted geothermal energy reserves in conductive systems in Macedonia (Popovski and Lund 1999)

No.	Hydro-geothermal system	Rocks + Water	Water
		max (Rg = 0, 1) 10^{15} J	max (Rg = 0, 1) 10^{15} J
1	Ovce Pole	7339.50	440.40
2	Tikves 1	66.40	4.00
3	Tikves 2	7445.60	446.80
4	Tikves 3	2207.00	132.40
5	Skopska kotlina	24.00	1.40
6	Strumicka kotlina	6.00	0.40
7	Kocanska kotlina	27.00	1.60
	Total	17115.50	1027.60

well-predictable spending in the initial period and good prospects for further steps. However, it is necessary to underline that the development of any geothermal energy resource depends not only on available reserves and development costs, but also (very much) on the availability of customers for the produced heat, able to ensure recovery of the initial investments and cover operating expenses (Popovski and Lund 1999).

Table 7 Predicted geothermal energy reserves in convective systems in Macedonia (Popovski and Lund 1999)

No.	Hydro-geothermal system	Rocks + Water	Water
		Max (Rg = 0, 1) 10^{15} J	Max (Rg = 0, 1) 10^{15} J
1	Skopska kotlina	3585.60	215.10
2	Proevci	14.90	0.90
3	Podlog	2976.60	189.90
4	Istibanja	3114.90	124.60
5	Bansko	3028.50	181.70
6	Kezovica	6744.70	38.70
7	Gevgelija	3114.90	186.90
8	Strnovec	23.90	1.40
9	Sabota voda	2.30	0.10
10	Toplik	19.40	1.20
11	Topli dol	7.80	0.50
12	Toplec	23.90	1.40
13	Rakles	1.50	0.10
14	Povisica	2221.50	133.30
	Total	18,780.40	1072.80

Conclusions

The most important advantage of geothermal energy is its domestic origin, independent of climate or seasonal changes or market drivers. The level of technology allows for large-scale utilization for either power or heat generation. On the other hand, the negative aspects are dependence on location, available temperature and flow of the resource, and long and capital-intensive initial period of development.

Even though not investigated enough, it is safe to say that Macedonia is relatively rich in hydro-geothermal energy, particularly its central and eastern parts. Thermal water temperatures are up to 78 °C, or below the minimum for power generation. However, reservoir temperatures estimated by means of geothermometers are about 100 °C or higher, meaning that more extensive research and exploration, and deeper drilling, might uncover higher temperatures.

Macedonia has a rich and long experience in geothermal energy use, with a broad range of application possibilities, reliable exploitation, and economy of use, despite the relatively obsolete technologies applied. If compared with other renewable energy sources, geothermal energy offers the highest reliability of supply and the lowest price of energy.

Geothermal energy can be the basis for large-scale development of out-of-season farming, drying of fruits and vegetables, central heating of residential, public and industrial buildings and facilities, and the development of spa and recreational tourism. In combination with fossil fuels and other renewable energy sources, it enables competitive production of electricity and heat.

Existing data, analyses and assessments of geothermal resources (energy and balneotherapy) in Macedonia corroborate that it is justifiable to proceed with broader and accelerated development.

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Mineral, Thermal and Thermomineral Waters of Bosnia and Herzegovina

Neven Miošić and Natalija Samardžić

Abstract Bosnia and Herzegovina, a country of Alpine orogene system, presents a terrain with a complex geological phenomenology and numerous mineral, thermal and thermomineral waters; there are 193 deposits of mineral, 57 thermal and 30 thermomineral waters with *ca* 400 natural springs and 170 drillholes and wells. The total yield of all deposits is 7,035 l/s, of which mineral waters contribute 4114 l/s, thermal 1828 l/s and thermomineral 1093 l/s. Drillings were performed in 50 deposits with natural springs and in 31 deposits without springs. Exploitation has been carried out in 47 deposits to establish the quality and quantity of these resources. The present use of mineral waters is in balneology, recreation, bottling and industrial use; thermal in balneology, recreation, bottling, water-supply, thermoenergetics and industrial use, and thermomineral in balneology, recreation, bottling, thermoenergetics and extraction of mineral raw materials. The total established power of 87 hydrogeothermal deposits is 251 MWt and potential power is *ca* 795 MWt with reference to 10 °C, while geothermal direct heat use is only about 22 MWt. Evidence clearly shows the potential of positive results of investigations and the sustainable and polyvalent use of these resources in numerous sites, though many obstacles make the feasibility of this application difficult. These waters are mostly renewable resources based on isotopic content and other data. There are a few waters of no meteoric origin in closed deep artesian horizons. All waters are dominantly prenuclear ("dead" waters—$^{3}H = 0$). According to ^{14}C content, a large number of waters are over 40,000 years old, with very slow circulation and long residence times in the aquifers, and they are naturally protected by insulating rocks as roof barriers to prevent any surface contamination of aquifers. Waters have various origins, content and concentration of constituents, and were formed in different rock ages and in complicated geological structures. There are specific waters of rare and effective physical and chemical composition which do not exist in surrounding countries. Mineral waters have a large range of TDS from

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N. Miošić
Dr. F. Bećirbegovića 19, 71000 Sarajevo, Bosnia and Herzegovina

N. Samardžić (✉)
Federal Geological Survey Sarajevo, Ustanička 11, 71210 Ilidža, Bosnia and Herzegovina
e-mail: natalija.samardzic@fzzg.gov.ba

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0.5 to 270 g/L, thermal from 0.15 to 0.8 g/L and the thermomineral from 1 to even 300 g/L; there is a great variety from the very acidic type (pH = 3) to hyperalkaline with pH = 12, with diverse contents of N_2, O_2, CO_2, H_2S composition with free and dissolved gases and different GWR. The CO_2 in most of the carbon acid waters, according to $\delta^{13}C$ in the CO_2, is created at great depths and probably originates by thermal hydrolysis of marine carbonate rocks. In some deposits, the existence of higher homologues of methane and values of $\delta^{13}C$ in CH_4 indicate an organic origin of CH_4 deriving from petroleum-gaseous deposits overlying ophiolitic rocks. Determining the plausible geological and geothermal models of terrain for the various types of groundwaters are basic theoretical and practical tasks, which allow the location of shallower wells for successful capturing of waters. Additional greater capacities of different groundwaters are possible to obtain by drillings of new deeper wells in almost all active mineral and hydrogeothermal deposits. It is of considerable interest to determine whether and in which sites and lithostratigraphic units there are as yet undiscovered hydrogeotherms of higher enthalpy in shallow and deeper horizons, particularly by investigating deposits with shallow drillings. Higher temperatures and greater yields have already been found in several deposits with shallow drillholes.

Keywords Hydrogeological characteristics · Water quality · Water genesis · Utilization · Bosnia and herzegovina

Introduction

Bosnia and Herzegovina (B&H) is situated in SE Europe in the Western Balkan region and bordering Croatia, Serbia and Montenegro. B&H belongs to the well-known geographical and geological Dinarides system with complex geological properties, different lithological composition of rocks which have resulted in the existence of numerous and various deposits of all three water types characterized by irregular distribution in space, different hydrogeological, physical and chemical characteristics, conditions of recharge, forming and discharge of their aquifers and various possibilities of current and potential use.

The waters occur mostly in the internal Dinarides i.e. in hydrogeological structures of artesian basins, intermountain depressions and folded areas (Fig. 1); in these zones there are mineral, thermal and thermomineral waters, while in the Outer Dinarides hydrogeological massifs of Mesozoic carbonate rocks have a small number of mineral waters only. Of 280 known deposits, 80 are insufficiently investigated, and 50 completely unexplored, so considerable scope exists for studying these natural resources. The abundance of water phenomena and their wide range of applications provide opportunities for multidisciplinary research to exploit these waters. Water use is very small in relation to the capacities of most deposits, so new wells will increase the capacity to exploit these waters.

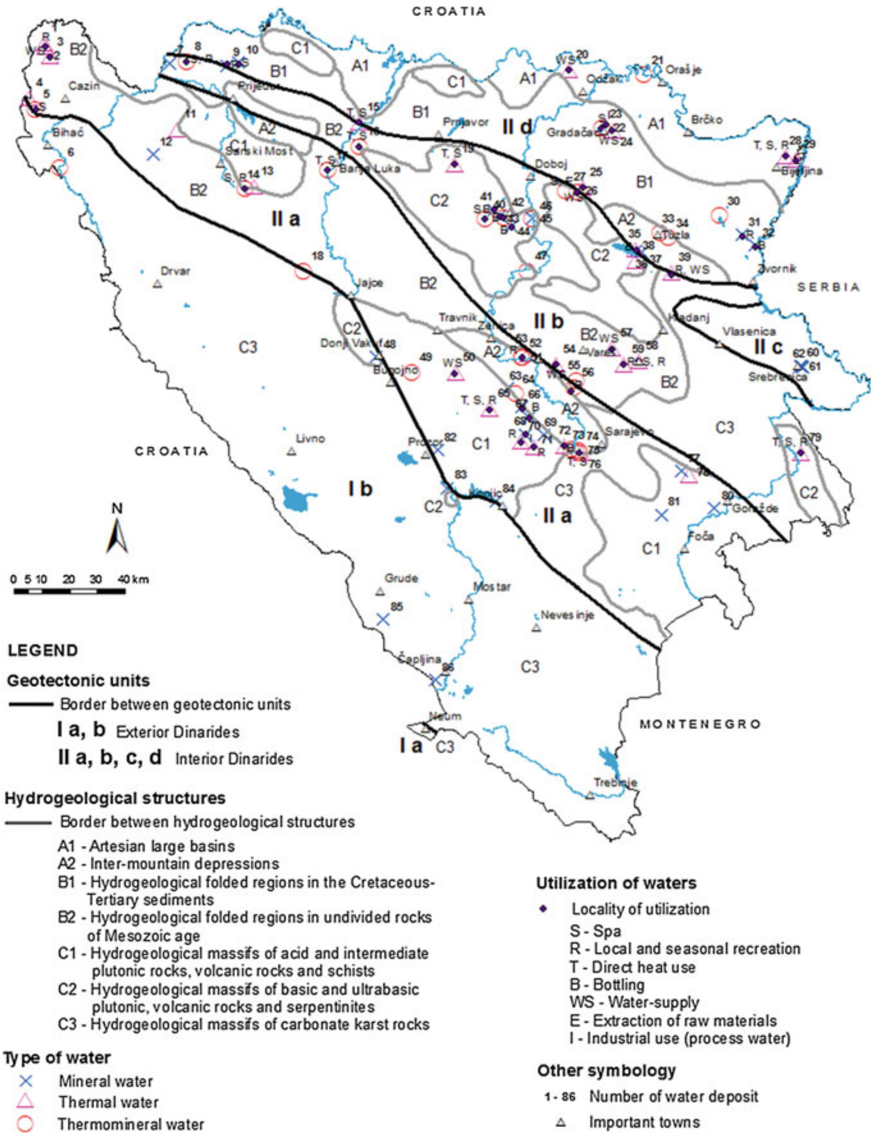

Fig. 1 Map of mineral, thermal and thermomineral waters of Bosnia and Herzegovina

Geological Background and Hydrogeological Structures

The terrain of Bosnia and Herzegovina belongs to parts of the External and Internal Dinarides and consists of the following geotectonic units (Petković 1961; Sikošek and Medwenitsch 1969; Papeš 1988):

- Outer Dinarides (I)—Zone of the Adriatic paraautochton (I a) and High karst zone (I b),
- Inner Dinarides (II)—Zone of Mesozoic limestones and Paleozoic schists (II a), Central ophiolitic zone (II b), Internal Paleozoic zone (II c) and Internal dinaric belt of horsts and troughs (II d).

High karst zone (nappe) is characterized by "great longitudinal faults with a structure strike from NW to SE" (Sikošek and Medwenitsch 1969) with overthrusts and tectonic windows. Massifs of a zone of Paleozoic schists and clastic rocks are overthrusted on a High karst zone along the lines of Bihać–Ključ–Jablanica–the source of the river Neretva.

The Paleozoic zone adjoins the Ophiolitic zone along the line Bosanski Novi–Banja Luka–Srednje–Goražde.

The Central ophiolitic zone is overthrusted on the Paleozoic zone; the boundary of the first zone toward the zone of horsts and troughs of northern Bosnia goes along the line Laktaši–Doboj–Lukavac–Zvornik, which is orographic, lithological and tectonic in the form of large faults.

The Internal Paleozoic zone occurs between Drinjača, Jadar and Drina rivers and is characterized with Paleozoic rocks and effusive Neogene volcanic rocks.

The Zone of horsts and troughs of northern Bosnia is characterized by elevations and deep depressions caused by tectonics including young and multiphase regenerated faults. Tectonic and structural–geological elements are the key players in the recharge, forming and discharge of accumulations of mineral, thermal and thermomineral waters.

These waters exist in terrains of different hydrogeological structures of Bosnia and Herzegovina, which are the consequence of complex geological-tectonic relations. The basic hydrogeological structures are the followings:

A_1—artesian large basins,
A_2—inter–mountain depressions,
B_1—hydrogeological folded regions in Cretaceous–Tertiary sediments,
B_2—hydrogeological folded regions in undivided rocks of Mesozoic age,
C_1—hydrogeological massifs of acid and intermediate plutonic rocks, volcanic rocks and schists,
C_2—hydrogeological massifs of basic and ultrabasic plutonic, volcanic rocks and serpentinites,
C_3—hydrogeological massifs of carbonate karst rocks.

Hydrogeological structures, resulting from various geological and tectonic relations, generally coincide with geotectonic units; they condition the diversity of waters in distribution, physical-chemical properties, genesis, water abundance, wide spaces and hydrodynamic parameters (Fig. 1).

Detailed information on the geology, hydrogeology and genesis of these waters is reported in Čičić and Miošić (1986), Josipović (1971), Katzer (1919), Miholić (1952, 1957, 1960), Miholić and Mirnik (1957a, b), Miošić (1977, 1980, 1981, 1982, 1987a, b, 2001), Papeš (1988, 2012a, b), Sikošek and Medwenitsch (1969).

Basic Hydrogeological Characteristics of Waters

The variety of geological and hydrogeological relations of rocks results in an irregular spatial distribution of springs mainly and closed deep aquifers. There are open, semiopen, semiclosed and closed hydrogeological systems with genetic diversity and diversity of component concentrations. Aquifers are characterized with a variety of horizontal and vertical discontinuities; thickness, depth and hydrogeological parameters.

Deposits of mineral waters with springs are the most numerous (159), with 31 thermal and only nine thermomineral deposits (Table 1). The potential power is over four times the current power, and this could be obtained by rehabilitation of active wells but mostly by drilling new deeper wells in about 60 deposits.

Mineral Waters

Mineral waters occur in rocks of diverse lithological composition and age and usually have a low yield, different chemical content with N_2, O_2, CO_2 and H_2S as the main gaseous components (Table 2). These waters are categorized as salt, sulfate-arsenic-iron, sulfate and mineral waters with CO_2.

Saline mineral waters are the Cl–Na-type with different mineralization (5–270 g/L) which exist in the wider region of Tuzla in Tertiary evaporite sediments and in areas of Majkic Japra, Hašani (spring rich with Glauber's salt), Donji Vakuf—P-T_1 sediments, Orahovica—Tc sediments and Gabela—Cretaceous rocks. The origin of these waters is mainly from dissolving salt evaporites and these are indicators of the existence of Na–K-salt layers.

Sulfate–arsenic–iron spring waters exist in hydrothermally exchanged Neogene dacite–andesite effusive rocks. They are altered and impregnated by various sulphide minerals in some 50 locations in the wider area of Srebrenica. Their accumulations occur in the oxidation zone in open structures and are developed in now-active electrochemical processes of meteoric origin; they are disturbed by mining activities. Mineralization of waters is diverse, ranging from about 285.5 mg/L (Vitlovac) to 5700 mg/L (Očna voda). Waters have a rare ionic composition—SO_4–$HAsO_4$, and are Mg, Ca, Na-types, pH 2–5. The content of iron in various sources is up to 2185 mg/L (Novi Guber), and arsenic up to 17 mg/L. Enrichments of microelements are significant (Cu = 50.5 mg/L in Očna water, Lisac Mn = 44.6 mg/L) (Miholić 1958). The yield of springs is in most cases low ($Q < 0.1$ l/s —Očna water to 5 l/s—Veliki or Crni Guber)—Miholić (1955, 1958). Oscillations of yield and chemical ingredients are in correlation with the pluviometric regimes in the spring catchment areas. These waters are rare and have effective physico-chemical components and are significant due to the high content

Table 1 Data on springs, drillholes/wells and water deposits

Type of waters	Deposits with springs only	Deposits with springs and drillholes	Deposits with drillholes only	Deposits with springs and drillholes/wells	Number of deposits	Yield of springs and drillholes/wells (l/s)	Present power of springs and drillholes/wells (MWt)	Possible power of springs and drillholes/wells (MWt)
Mineral	159	16	18	34	193	4114		
Thermal	31	18	8	26	57	1828	106.8	315.4
Thermomineral	9	16	5	21	30	1093	144.6	479.8
Total	199	50	31	81	280	7035	251.4	795.2

Table 2 Significant deposits of mineral, thermal and thermomineral waters

No on map	Name	Locality	Yield (l/s)	T (°C)	Power (MWt)	Litostratigraphy of aquifers	Water type	M (mg/L)	Gaseous
Mineral water									
7	Spring Smrdeljac	Cerovica–Bosanski Novi	0.3	12		Conglomerate, sandstone, marl (M)	SO_4–HCO_3–Ca	2758	H_2S
9	Spring	Jelovac Bosanska Dubica	1	12		Sandstone, marl (Tc)	SO_4–HCO_3–Ca	1123	H_2S
10	Spring and well	Mlječanica Bosanska Dubica	10	13.1		Sandstone, marl (Tc)	SO_4–Ca	2539	H_2S
12	Spring and drillholes	Majkić Japra	1	14		Sandstone, marl (P, T)	Cl–Na–Ca	28,487	
31	Springs and drillholes	Jesenica–Zvornik	0.8	12		Sandstone, marl, conglomerate (E)	HCO_3–Cl–Na	4120	CO_2
32	Well	Kozluk–Zvornik	3.5	14		Clastic sediments, carbonates (K, Tc)	Cl–HCO_3–Na	3726	CO_2
36	Spring Kiseljak and well	Bokavić Ševar–Tuzla	1.0	13.8		Serpentinite, VSS[a]	HCO_3–Mg–Na	2266	CO_2–N_2
37	Spring and wells	Ljubače–Mlin	7	12		Sand, gravel (al)	HCO_3–Mg	4355	CO_2
41	Spring Slatina and well	Orašje Planje–Tešanj	0.3	15.5		VSS, spilite	HCO_3–Na–Mg	2818	CO_2
43	Spring Kiseljak and wells	Raduša–Tešanj	8	12.5		Dijabaze, VSS	HCO_3–Cl–Ca–Mg	7866	CO_2
44	Spring Kiseljak and drillhole	Crni Vrh–Tešanj	0.2	13.5		Spilite, chert, sandstone, claystone (VSS)	HCO_3–Na–Mg	3158	CO_2
45	Spring, drillhole and dig well	Moševac–Maglaj	1	14.9		Serpentinite, chert (VSS)	HCO_3–Mg–Na	4819	CO_2
46	Spring	Rječica–Maglaj	0.1	15.4		Chert, conglomerate, VSS	HCO_3–Mg–Na	3920	CO_2

(continued)

Table 2 (continued)

No on map	Name	Locality	Yield (l/s)	T (°C)	Power (MWt)	Litostratigraphy of aquifers	Water type	M (mg/L)	Gaseous
48	Spring Slanac	Donji Vakuf	0.01	12		Limestone, clastic sediments (P, T)	Cl–Na	13,695	N_2
60	Spring Novi Guber	Srebrenica	2.2	14		Dacite–andesite (Tc)	SO_4–Fe–Al	3196	N_2
61	Spring Crni Guber	Srebrenica	5	13		Dacite–andesite (Tc)	SO_4–Al–Fe	778	N_2
62	Spring Očna voda	Srebrenica	0.5	11.4		Dacite–andesite (Tc)	SO_4–Ca–Mg	5732	N_2
63	Springs and wells Klokoti	Klokoti–Kiseljak	10	11		Sand (al)	HCO_3–Na + K–Fe	80–220	CO_2
66	Well BM-1	Fojničko–Kiseljak	7.3	12		Conglomerate, sand (M)	HCO_3–SO_4–Ca–Na	1030	CO_2
67	Springs and wells Sarajevski kiseljak	Kiseljak	15	12		Limestone, dolomite (T)	HCO_3–SO_4–Ca–Na–Mg	6403	CO_2
68	Spring Komarac	Alagići–Kreševo	50	10		Limestone, sandstone (T1)	SO_4–HCO_3–Ca	930	
69	Spring	Boljkovići–Lepenica	0.1	11.5		Clastic sediments, limestone (T)	SO_4–HCO_3–Ca	2651	CO_2
77	Spring Kiseljak	Prača	0.1	14.5		Clastic sediments (C)	HCO_3–Ca–Na–Mg	2166	CO_2
80	Spring Kiseljak	Odska Potok–Bogušići	0.05	15.2		Clastic sediments (Pz)	HCO_3–Ca–Na–Mg	1711	CO_2
81	Spring and drillholes	Donje Selo–Jabuka	0.1	11.1		Clastic sediments, limestone (P, T)	SO_4–HCO_3–Na–Mg	3040	CO_2
82	Spring Rika	Ljubunci–Prozor	20	9.1		Limestone, dolomite, gypsum (T)	SO_4–Ca (–Mg)	1300–2213	N_2
83	Spring Smrdelj	Slatina–Jablanica	2	11		Shale, clastic sediments (T1)	SO_4–HCO_3–Ca	1448	H_2S
84	Spring Slani izvor	Orahovica Konjic	2	11.2		Clastic sediments (T1)	Cl–HCO_3–Na–Ca	1643	N_2
85	Spring Klokun	Klobuk–Ljubuški	2000	12		Limestone, dolomite (T, K)	SO_4–HCO_3–Ca	1177	N_2

(continued)

Table 2 (continued)

No on map	Name	Locality	Yield (l/s)	T (°C)	Power (MWt)	Litostratigraphy of aquifers	Water type	M (mg/L)	Gaseous
86	Spring Slani izvor	Gabela–Čapljina	2–4	11		Limestone (K)	Cl–Na	5691	N_2
Thermal water									
1	Springs and wells	Barake–Mala Kladuša	40	22.5	2.092	Dolomite (T, K)	HCO_3–Ca–Mg	427	N_2–O_2
2	Spring Toplik and Well MKH-1	Mala Kladuša–Grabovac	150	27	10.671	Dolomite (T, K)	HCO_3–Ca–Mg	552	N_2–O_2
3	Spring and well	Donji Šmatac–Mala Kladuša	150	22	7.533	Dolomite (T, K)	HCO_3–Ca–Mg	350	N_2–O_2
4	Springs and Wells	Tržačka Raštela	50	17	1.464	Limestone (T)	HCO_3–Ca–Mg	445	N_2–O_2
11	Spring Ilidža	Budimlić Japra	15	18	0.502	Limestone (P, T)	HCO_3–SO_4–Ca–Mg	451	N_2–O_2
13	Springs Ilidža	Kozica–Sanski Most	6	25.3	0.384	Limestone (P, T)	HCO_3–Ca–Mg	385	
15	Springs and Wells	Laktaši	100	30	8.370	Limestone (T)	HCO_3–Ca–Mg	790	CO_2–N_2
19	Springs and Wells	Kulaši–Prnjavor	20	30	1.674	Diabase + peridotite (VSS)	CO_3–SO_4–Cl–Na–Mg	128	N_2–CH_4
20	Well BV-1	Vrbovac–Odžak	17	17	0.498	Limestone (M)	HCO_3–Ca	629	
22	Wells K-1, HE-1, EB-1, BMI-2	Industrijska zona–Gradačac	25	18–31	1.253	Limestone (M)	HCO_3–Ca	800–1000	
24	Springs and Wells	Mionica Krčevine–Gradačac	30	18.5	1.255	Limestone (M)	HCO_3–Ca	600	
25	Well P-2	Seljanuša–Gračanica	9	17	0.264	Limestone (Pc)	HCO_3–SO_4–Ca–Mg	450	
28	Drillhole S-1	Dvorovi–Bijeljina	7	75	1.904	Limestone (K)	HCO_3–Cl–Na–Mg–Ca	600	N_2–CO_2–O_2

(continued)

Table 2 (continued)

No on map	Name	Locality	Yield (l/s)	T (°C)	Power (MWt)	Litostratigraphy of aquifers	Water type	M (mg/L)	Gaseous
29	Drillhole GD-2	Slobomir	35	75	3.66	Limestone (T)	HCO_3–Na + K		
35	Well BM-2	Bokavić Ševar	0.1	19.5	0.003	Sandstone (VSS)	CO_3–Cl–HCO_3–Ca–Mg	213	
38	Spring	Šerići–Živinice	0.03	15.8	0.0007	Peridotite (VSS)			
39	Springs Toplica and wells	Spreča–Živinice	230	24.8	14.245	Limestone (T)	HCO_3–Ca–Mg	452	N_2
50	Spring Ilidža and Wells	Kruščica–Vitez	10	19.2	0.385	Limestone (Pz)	HCO_3–Mg–Ca	491	
53	Spring and wells	Ribnica–Kakanj	70	29	5.566	Limestone (K, Tc)	HCO_3–SO4–Ca	867	
54	Spring Ilidža and wells	Kraljeva Sutjeska	20	21	0.92	Limestone, sandstone (K)	HCO_3–SO_4–Mg–Na	560	
57	Spring	Očevlja–Vareš	16	25.8	1.057	Limestone (T)	HCO_3–Ca	280	
58	Springs and Wells	Olovo	80	34	8.035	Limestone (T)	HCO_3–Ca–Mg	450	
59	Springs	Orlja	3,5	25	0.186	Limestone (T)	HCO_3–Ca	366	
65	Springs and Wells	Fojnica	250	22.6	11.890	Marbled dolomite (Pz)	HCO_3–Ca–Mg–Na	505	CO_2–N_2
70	Springs Banja	Kreševo	18	17	0.527	Limestone, dolomite (Pz)	HCO_3–Ca–Mg	370	
71	Springs	Toplica–Lepenica	18	20	0.753	Limestone, dolomite (Pz)	HCO_3–SO_4–Ca–Mg	340–580	
72	Well Coca-Cola	Mostarsko raskršće–Hadžići	32	18	1.071	Limestone, dolomite (T)	HCO_3–Mg–Ca	420	
76	Drillhole IB-7	Butmir	30	22	1.506	Limestone (T)	HCO_3–Ca–Mg	300	
78	Springs	Čeljadinići	100	15	2.092	Limestone (S, D)	HCO_3–Ca	420	
79	Springs and wells	Višegradska banja–Višegrad	80	34	8.035	Limestone (T)	HCO_3–Ca–Mg	442	N_2–O_2

(continued)

Table 2 (continued)

No on map	Name	Locality	Yield (l/s)	T (°C)	Power (MWt)	Litostratigraphy of aquifers	Water type	M (mg/L)	Gaseous
Thermomineral water									
5	Springs and wells	Gata	30	36	3.264	Dolomite (T)	SO_4–Cl–HCO_3–Ca–Na–Mg	1500	N_2–CO_2
6	Spring Svetinja	Račić–Bihać	1,5	19	0.056	Limestone (K)	SO_4–HCO_3–Cl–Ca–Mg	1074	
8	Springs and well	Lješljani–Bos. Novi	7	32	0.644	Peridotite (VSS)	Cl–Na–Ca	2113	CH_4–N_2
14	Springs and wells Sanska Ilidža	Ilidža–Sanski Most	40	32	3.682	Limestone (P, T)	SO_4–Ca	2500	N_2–O_2
16	Springs and wells	Slatina–Banja Luka	100	44	14.229	Limestone + sandstone (VSS)	SO_4–HCO_3–Ca–Mg	2900	CO_2
17	Springs and wells	Gornji Šeher Banja Luka	150	35	15.693	Limestone + dolomite (T)	HCO_3–SO_4–Ca–Mg	1300	CO_2–N_2
18	Spring	Balkana–Mrkonjić Grad	3	17	0.087	Limestone (T)	SO_4–HCO_3–Ca	1111	
21	Well Do-1	Domaljevac–Bosanski Šamac	20	96	7.198	Limestone (K)	Cl–SO_4–HCO_3–Mg–Ca	11,120	CO_2–N_2
23	Springs and wells	Gradačac	50	30	4.185	Limestone + sandstone	HCO_3–SO_4–Na–Ca	1100	N_2
26	Springs and wells	Sočkovac	250	39	30.341	Limestone (T)	HCO_3–Ca–Na + K–Mg	4119	CO_2
27	Spring Kiseljak and well	Boljanić–Spreča	5	25	0.313	VSS	HCO_3–Na–Ca	3000	CO_2
30	Springs Rasol and drillholes	Priboj	3	24	0.175	Sandstone (Tc)	Cl–SO_4–HCO_3–Na	3794	N_2–CO_2–H_2S
33	Wells	Slatina–Tuzla	30	27	2.134	Limestone + sandstone (Tc)	Cl–Na	267,584	N_2–CH_4

(continued)

Table 2 (continued)

No on map	Name	Locality	Yield (l/s)	T (°C)	Power (MWt)	Litostratigraphy of aquifers	Water type	M (mg/L)	Gaseous
34	Drillhole Sl-1	Slavinovići–Tuzla	4	34.5	0.410	Limestone + sandstone (Tc)	Cl–HCO_3–Na	6414	CH_4–CO_2–N_2
40	Spring and well -Banja Vrućica	Teslić	20	38	2.343	Limestone + sandstone (T)	HCO_3–Cl–SO_4–Na–Ca–Mg	3700	CO_2
42	Wells	Dolac–Tešanj	0.3	22	0.015	Diabase, chert, sandstone, claystone (VSS)	HCO_3–Cl–Na–Mg–Ca	5239	CO_2
47	Spring Kiseljak and drillholes	Bistrica–Žepče	2	20	0.083	Peridotite (VSS)	HCO_3–Mg–Ca	4260	CO_2
49	Springs and drillhole Vruća voda	Vitina–Bugojno	1	25.5	0.064	Limestone (T)	SO_4–Ca–Mg	1040	
51	Spring and drillhole IT-1	Tičići–Kakanj	35	56	6.737	Limestone (K, Tc)	HCO_3–SO_4–Ca–Na	1074	CO_2–N_2
52	Spring and drillhole IT-2	Radići–Kakanj	22	39	2.670	Limestone (K, Tc)	HCO_3–SO_4–Ca–Na	1968	CO_2–N_2
55	Springs	Dabravine	1	12–16	0.017	Clastic sediments, limestone (K)	HCO_3–Ca	2596	CO_2
56	Springs Sedra	Breza	30	19.3	1.167	Limestone (K)	HCO_3–SO_4–Ca–Mg	1260	CO_2
64	Drillhole DB-1	Biohan	0.1	17.5	0.003	Sandstone (Pz)	HCO_3–Cl–SO_4–Na	15,673	CO_2
73	Springs Kiseljak and Well	Blažuj	20	24	0.700	Limestone + dolomite (T)	HCO_3–SO_4–Ca–Mg	2439	CO_2
74	Drillhole IB-10	Ilidža–Sarajevo	27	20	1.199	Limestone (T)	HCO_3–Ca	1302	CO_2
75	Springs and Wells	Ilidža–Sarajevo	260	57.6	48.00	Limestone (T)	HCO_3–SO_4–Cl–Ca–Na–Mg	4140	CO_2–H_2S

[a] VSS-volcanic-sedimentary series

of iron, arsenic, trace elements and elevated radioactivity (Rn = 133 Bq/L); they are similar to the well-known waters in Levico, Italy.

Sulfate waters with H_2S exist around Bosanski Novi, Bosanska Dubica, Prijedor, Ključ–Šipovo, the Central Bosnia basin, Jablanica, Kozluk, Tuzla, Alagići, Prozor and Klobuk; the last three sites are without H_2S. The waters are the SO_4–HCO_3–Ca–Mg-type with mineralization to 3 g/L. They are formed by gypsum dissolution in P–T_1 evaporites in shallow zones. CO_2 is of deeper origin, while H_2S arose by reduction of sulfates or biogenic processes. The most important springs are in Jelovac and Mlječanica (Bosanska Dubica), where pumping tests of wells gave a yield over 10 l/s. Mineralization of these waters is 460–1300 mg/L with exhalations of free H_2S. These waters are formed by dissolution of Tertiary sulfate evaporites.

Mineral waters with CO_2 occur in Tertiary sediments of northern Bosnia, the ophiolitic zone, massif of Central Schist Bosnian Mountains and in the inner Paleozoic zone and Paleozoic rocks of SE Bosnia. All occurrences are characterized by a HCO_3–Ca–Mg composition with mineralization from 1 to 8 g/L, increased content of free CO_2 (500–2000 mg/L), and water temperatures are similar to the mean annual air temperature of analogous locations. CO_2 is of deeper thermogenic–thermolitic or shallow chemical origin. Yields of springs and drillholes are different and range from 0.1 to 20 l/s.

The greatest number of occurrences of these waters is registered in the ophiolitic zone and along the contact of this zone and hydrogeologically folded areas of northern Bosnia around Tešanj, Teslić, Žepče, Maglaj, Sočkovac, Bokavić Ševar. Yields of springs are regularly very low ($Q < 0.5$ l/s). Most waters are the HCO_3–Ca type with different amounts of other cations and mineralization of 2–8 g/L. All springs occur in tectonic contacts with rocks of various lithologies. Low circulation along fracture systems of numerous faults in ophiolitic insulator complexes cause small yields of springs.

The most important occurrences are along the well-known Busovačka fault zone at the contact of the hydrogeological massif of Paleozoic schists and intermountain depression of Tertiary sediments of central Bosnia from Busovače to Blažuj. Here, there are over 30 springs and a considerable number of sites with exhalations of CO_2 only. The most important springs are situated in Kiseljak with several wells of different water and gas composition with greater yields of waters and CO_2 and high pressure of free CO_2 (Bać 1957). Great exhalations of CO_2 are in Klokot and Bilalovac, where these waters have a low mineralization to 200 mg/L. Here, CO_2 ascends along young faults, and water is contemporary of meteoric origin in alluvium and Pliocene sediments. Due to the slow circulation of waters to the springs, the Rn content is low, while the drillholes with fast water circulation and minor decay time, Rn concentration is higher. Thus, Rn originates from Palaeozoic rocks (Miholić 1960). Water springs also occur in numerous sites (Prača, Bogušići, Jabuka, Koluna, Čajnice, Međuriječje etc.) in the Paleozoic massif of SE Bosnia in the mining zones with lead, zinc, iron, gypsum and anhydrite, which reflect the water chemical characteristics.

Thermal Waters

Thermal waters exist mainly in hydrogeological massifs of Mesozoic and Paleozoic rocks; springs are in the areas of old, deep, reactivated and young faults. Primary aquifer is mostly of carbonate rocks of Triassic age; they have a different cationic Ca-M-Na-type, monotonous anionic (HCO_3) composition (with exception of hyperalkaline waters), N_2–O_2 gas composition, low mineralization water (300–600 mg/L) with an average of about 500 mg/L. They are characterized by slow water exchange, a large yield of accumulations—there are springs and wells giving over 200 l/s (Fojnica, Mala Kladuša, Toplica); the most productive aquifers are Triassic limestones, but there are springs with very low yields $Q < 1$ l/s in the Ophiolitic zone (Vaićeva voda, Šerići).

There are several water occurrences in the Una-Sana Paleozoic zone from Triassic carbonate rocks; three abundant deposits with deep wells are in the area of Mala Kladuša with large yields and water temperature up to 29 °C. However, higher water temperatures are obtained in two deposits in shallow zones and lower in deeper horizons, which is a consequence of the existence of two separate reservoirs in vertical sequence formed by overthrusting of older (Triassic) on younger (Cretaceous) rocks. Hypothermal waters in Tržačka Raštela and the Bihac basin occur in proximity to strong karstic water springs. A strong spring with more wells in Triassic aquifers, $t = 29$ °C is in Laktaši. Waters from Cretaceous carbonate rocks are in the northern edge of the Central Bosnia basin, in an artesian basin around Gradačac from Neogene sediments, in Prača from Devonian carbonates and in Semberija (S-1—Dvorovi and GD-2—Slobomir) from Cretaceous and Triassic limestones.

Hypothermal hyperalkaline waters are in the Ophiolitic zone, in the Spreča fault zone (Vlajići, Gracanica, and Prošići) and as the most important deposit in Kulaši, which has the highest temperature (30 °C), where larger amounts of water were obtained by wells. These waters have a low mineralization (150 mg/L) and $pH = 10$–12.

Thermal waters Kruščica, Fojnica, Kreševo and Lepenica are in the Middle Bosnian Paleozoic massif ascending along the fault communications; their aquifers are in carbonate rocks, which are covered by discontinuous Paleozoic insulators. Two separate reservoirs of different yields, hydraulic regime, temperature and chemical content are at Fojnica. The waters are close to each other. Spring waters circulating through tufa sediments are enriched with high Rn content ($Rn_{max} = 643$ Bq/L) only, which is secondary, accumulated in tufa recent spring sediments and not in bedrock rocks. Because of this, Rn values in waters in drillholes are very low (Miholić 1956, 1960).

Very abundant accumulations with numerous springs of thermal waters occur all over the Ophiolitic zone (Ponikva, Očevija, Solun, Orlja, Kovačići, Olovo, Knežina, Rogatica, Visegrad, Drinjača, Živinice). Water wells were made in Olovo, Toplica—Živinice and Višegrad spa, which resulted with artesian and subartesian sources. These waters are characterized by high yields from Triassic carbonate aquifers, which are overlain by volcanic-sedimentary insulator rocks. Toplica springs emerge from the carbonate massif of Romanija in contact with the Ophiolitic zone and horsts and troughs of northern Bosnia. Drilling in Višegrad spa in 1976 in B&H showed for the first time ultramafites and basic plutonites, volcanites and a diabas-chert formation. These present one chronostratigraphic horizon and lie discordantly on Triassic carbonate primary aquifers of thermal waters, as is the case in other parts of the Ophiolitic zone in B&H and Serbia (Papeš et al. 2012a). A maximum activity of Rn = 673 Bq/L (Miholić 1957) was registered here in spring waters issuing from tufa sediments in this spa, though not in water wells in primary aquifers (Miošić 1979).

Thermomineral Waters

Thermomineral waters are formed in large artesian basins, folded structures and hydrogeological massifs of the Internal Dinarides. Aquifers have roof insulator rock barriers with distinct vertical and horizontal discontinuities in space. Water exchange is very slow, mineralization often high, water is abundant with significant content of gases, and brines exist in some sites exist (Tuzla). They are characterized by an artesian hydraulic mechanism of accumulations, as well as considerable depths of primary aquifers. These waters according to macro-component composition are overwhelmingly hydrocarbonate with mineralization from 2 to 8 g/L, often with a high GWR of noncombustible and combustible gases.

Salt waters in the Tuzla area, found in springs and wells in Neogene sediments, are sedimentogene-relict and less of meteoric origin. Pumped waters from these wells have high mineralization, up to 300 g/L, and a temperature of 27 °C, of the Cl–Na-type. Increase of karstification of dissolved salt deposits has caused subsidence of Tuzla town, which lies on the salt layers. Artificial leaching of salt water deposits through wells has enabled the controlled use of saline solutions in the area of Tetima near Tuzla and prevented subsidence of the terrain of this town.

Drilled hydrocarbonate waters in Domaljevac (Posavina) in Triassic carbonate rocks (well Do-1) provide artesian thermomineral waters of high yield, high temperature and N_2–CO_2 gases. Hydrocarbonate–sulfate water in Ilidža—Gradačac issuing from the fault zone from Sarmatian and Tortonian sediments, and in the same sediments 300–1000 m farther were drilled thermal waters, which are in interference with the first waters, and this affects the quality and use of both waters.

Thermomineral waters with CO_2 exist as springs in Slatina, Teslić, Boljanić, Sočkovac, Blažuj and Ilidža. All of these deposits have drillholes/wells with large capacities of waters with free CO_2. Especially high capacities of artesian waters were obtained in Sočkovac in additional wells, which have mutual hydraulic interference. Waters have similar physical and chemical compositions, contents of free CO_2 (1500–2000 mg/L) with GWR = 2.5. These phenomena represent the greatest accumulations of thermomineral waters in B&H with CO_2, having 99 % pure CO_2. Triassic limestones are primary aquifers overlain by impervious

Ophiolitic rocks as roof barriers, which represent a single chronostratigraphic horizon, established in 1976 by J. Papeš in Višegrad spa (Papeš et al. 2012a).

A thermomineral water with CO_2 and H_2S in Ilidža near Sarajevo is a specific and interesting occurrence, being the only one of this kind in Bosnia and Herzegovina, with high yields of wells (Q = 100 l/s) and the same temperature of 58 °C in springs and wells. Near this water are CO_2 waters t = 20–30 °C (B-10A) and 24 °C (Blažuj) and a thermal water (Butmir) (Bać 1957). Well IB-10 has separated different water horizons with CO_2 and a large temperature inversion (t = 38 °C at 550 m and t = 20 °C at a depth of 1100 m, Q_{pump} = 86 l/s) and substantially reduced mineralization and content of CO_2 associated with depth (Miošić et al. 2013).

Tičići and Radići in the NE part of the Middle Bosnian basin in a fault zone have transient aquifers in K sediments and the primary probably in Triassic limestones. These give high yields and considerably higher temperatures compared with springs which were obtained in shallow drillholes; the last case being very rare in B&H.

Other waters exist as springs in Gata Ilidža, Sanska Ilidža, Gornji Šeher, Bugojno and Lješljani. The first three deposits belong to radioactive waters and have other natural features making them valuable balneological–therapeutic agents, and drillings gave large amounts of artesian waters. Longterm pumping tests of three wells in Sanska Ilidža (t = 30 °C) resulted in cessation of springs of thermal waters in Kozica (t = 23–25 °C), located about 4.5 km east of Sanska Ilidža. At the same time, a decrease of outflow in the wells, mineralization and water temperature was not registered (Papeš et al. 2012a). The only deposit of thermomineral hyperalkaline (pH = 11.5) water in B&H occurs in Lješljani. Water emerges from peridotites in the Ophiolitic zone along the fissures in which considerable convective cooling of water occurs. This is caused by the small yield of the spring—temperature at the bottom of the well at 670 m depth was 34 °C and the spring at the surface 30 m from SB-1 had, before drilling, a temperature of t = 18 °C and Q = 0.5 l/s. CH_4 and water are probably from the the primary aquifer in the footwall of Ophiolitic rocks from gas-oil horizons.

Physical and Chemical Features of Waters

The macro-component ionic composition of most of the selected 86 water deposits is of the Ca–HCO_3-type. Twelve mineral, 21 thermal and 13 thermomineral waters have Ca cation with more than 50 % mg-eq/L, while 12 mineral, 20 thermal and 10 thermomineral waters have more than 50 % of HCO_3 (Table 2; Fig. 2). Mineral and thermomineral waters have very different compositions, while thermal waters are much more uniform, with the HCO_3–Ca(Mg)-type prevailing (A section of Piper diagram). This ionic type is characteristic of waters which have the primary and transient aquifers in limestones and dolomites with a great variety of ages from the Paleozoic to Neogene; waters are rarely HCO_3–SO_4(Cl)–Ca(Na + K)–Mg-types. All these waters are characterized by normal pH values. The temperature of mineral

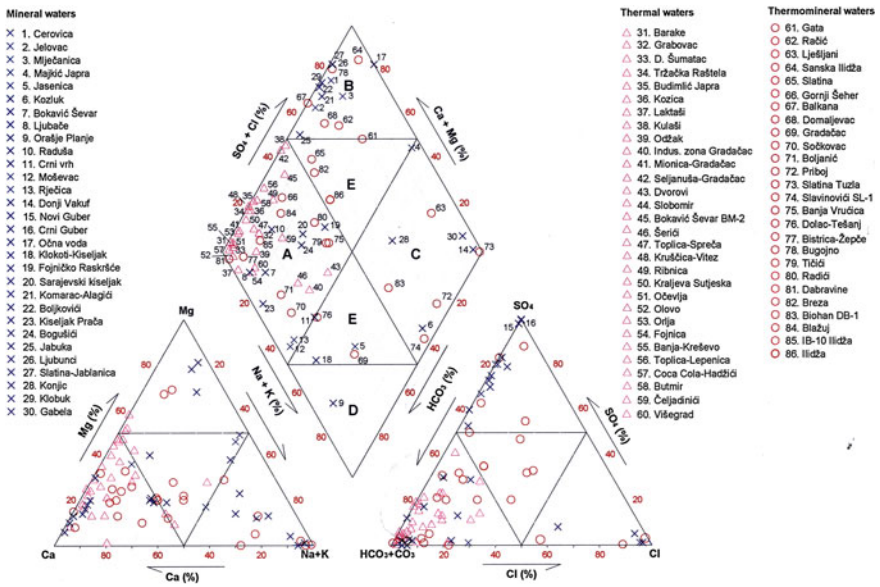

Fig. 2 Piper trilinear diagram of mineral, thermal and thermomineral waters of B&H

waters are in the range of 9.1–15.5 °C, thermal from 17 to 75 °C, and thermomineral from 17 to 96 °C.

The hyperalkaline thermal waters of Kulaši (CO_3–SO_4–Cl–Mg–Na-type, pH = 12), Bokavić Ševar (CO_3–Cl–HCO_3–Ca–Mg, pH = 9.4) and Šerići (pH = 11) are quite different from those described previously, because they occur in basic and ultramafic rocks of the Central Ophiolite Zone. Very rare specific acid waters of the Srebrenica area in Neogene volcanic rocks are SO_4–Fe–Al and Ca–Mg types with pHs from 2 to 4 and temperatures 11–14 °C.

Mineral and thermomineral waters have HCO_3 and SO_4 anions prevailing, while 7 waters contain only with Cl and Cl–HCO_3 anions. Four of these are mineral (Donji Vakuf, Majkić Japra, Gabela and Konjic) and 3 thermomineral (Tuzla, Ljesljani and Slavivovići). Some thermomineral waters are characterized by the presence of all three anions (Biohan, Ilidža, Račić, Priboj, Domaljevac). Ca and Na + K cationic compositions are the most common, while only one thermal water (Domaljevac) and 3 mineral waters (Bokavić, Raduša and Ljubače) have a dominant Mg cation. The waters of Crni Vrh, Moševac and Rjećica have Mg–Na cation compositions and three cations with more than 20 % mg eq/L are presented in the waters of Gata, Teslić, Sočkovac, Dolac–Tešanj and Ilidža.

Salt waters of the Cl–Na(Ca) type have the greatest mineralization, such as Majkić Japra (28.5 g/L), Donji Vakuf (13.7 g/L), Tuzla (270 g/L) and some waters of Domaljevac (11 g/L) and Biohan (15.7 g/L), which have the types Cl–SO_4–HCO_3–Ca–Mg and HCO_3–Cl–SO_4–Na. The lowest mineralization (80–220 mg/L) is represented by the thermal hyperalkaline waters of Kulaši, Bokavić Ševar and Šerići and the mineral HCO_3 water enriched with CO_2 in Klokoti.

The Piper diagram (Fig. 2) shows that only one mineral water in Orašje Planje occurs in section D. The waters, in which the content of HCO_3 anion is higher than 50 % mg eq/L, mostly with Ca and Ca–Mg cationic compositions, are in section A, while in part B are the most frequent waters of SO_4, Ca (Mg) and SO_4–HCO_3–Ca (Mg)-types, except Domaljevac which is of the Cl–SO_4–HCO_3–Ca–Mg-type. Water with a dominant Cl anion and Na cation are concentrated in section C and the waters in section E have different ionic compositions.

The mineral waters with the highest content of HCO_3 are waters enriched with CO_2 in various geological rock masses, while the SO_4 waters usually have N_2, and H_2S gas content. The waters with gases CH_4 and N_2, excepting hyperalkaline thermal waters, are predominantly of the Cl–Na-type (Tuzla, Lješljani, Slavinovići) and represent waters of artesian closed deep hydrogeological structures in Mesozoic and Tertiary rocks.

Genetic Characteristics of Waters

Analyses of stable and radioactive isotopes of waters and gases performed in *ca* 40 significant deposits after 1970 have improved our understanding of earlier findings and allowed contemporary explanations of genetic characteristics of waters and gases. These analyses were done by the Institute "Jožef Stefan"–Ljubljana (Pezdič et al. 1976–1990) and Institute "Ruđer Bošković"–Zagreb (Obelić et al. 1976–1990). All waters were predominantly old meteoric waters with low speed of recharge and greater residence times in the aquifers. Isotopic composition of oxygen and hydrogen indicates the condensation of water vapor at lower temperatures than today, which indicates recharge of water accumulations from higher altitudes and not from the glacial period. Meteoric water descends to depths of even 5000 m below the ground surface as indicated by earthquake foci depths (Ilidža). There are a few waters of non-meteoric origin in closed deep artesian horizons (Do-1—Domaljevac, Sv-1—Semberija, brines in wells around Tuzla, Biohan), which probably represent old fossil-relict waters (Fig. 1).

Mineral and thermomineral waters with CO_2 occur in various geological environments and have CO_2 of thermogenic origin. There are deposits with joint genesis of H_2O and CO_2 and reservoirs with independent generation of CO_2 and H_2O, where CO_2 has a deeper origin than the descent of meteoric waters.

$\delta^{13}C$ from −5 to −0,18 ‰ in areas of numerous mineral and thermomineral waters with CO_2 in Central Bosnia demonstrate a lithogenic origin of CO_2 by decomposition of Triassic and Paleozoic marine carbonate rocks in the basement of the Ophiolitic zone or genesis from even deeper zones. Fluids emerge circulation through privileged fault, which are the paths of convective ascension and efflux of waters and CO_2 exhalations. Their considerable age is also demonstrated by their ^{14}C contents (from 5000 to more than 40,000 years) (Miošić 1987a).

Meteoric waters do not disturb the isotopic composition of CO_2, which is unchangeable, i.e. various water types have an identical origin of CO_2. This means water and gas have different origins. Waters with predominantly N_2 are of different origin, and the CO_2 in them would be HCO_3 of fresh water, meteoric and sometimes thermogenic. H_2S in waters would be biogenic from anaerobic bacteria, from sulfate evaporites, pyrite oxidation products or from other oxidation-reduction reactions.

Water and gases with hydrocarbons prevailing were formed in artesian closed structures in Bosnian Posavina, Semberija, Tuzla basin and the Central Bosnian basin. They are overlain by thick roof insulators of Tertiary sediments, where water exchange is very slow. The existence of independent water horizons at various depths has been established in numerous deposits by drilling, where there is no mixing of waters under natural conditions.

Status and Results of Investigations

The first researchers of mineral, thermal and thermomineral waters in B&H were the Austro-Hungarian chemist Ludwig (1893) and geologist Katzer (1919). They performed the first physical and chemical water analyses with geological data, utilizing and explaining water genesis. Josipović (1971) made the first study of waters in Bosnia and Herzegovina with emphasis on water genesis. Miholić S., an eminent researcher of waters and geochemist, from 1938 to 1960 made an enormous contribution to our understanding of numerous waters, applying world-class scientific experiences with explanation of the genesis of major ingredients of waters. J. Bać investigated waters in numerous deposits by drillings over more than 50 years of active work. N. Miošić was the author of the first Map of mineral, thermal and thermomineral waters of B&H with an explanation and catalogue of all deposits. He led multidisciplinary investigations of 15 water deposits from 1975 to 2005, applying the latest methods available to the terrain in B&H, including isotope analyses. Among 50 deposits with springs, in 44 of them much greater yields were obtained in relation to analogous springs by drilling (Table 3). Waters with higher temperatures are obtained only in convective systems of thermomineral water deposits (Miošić 2001).

The power of 31 deposits of thermal waters with springs amounted to 12 MWt, though thermomineral waters in 9 deposits gave only 1.65 MWt. The total power of all drillholes was 237.76 MWt. This demonstrates that there is no effective use of waters without drillings, thereby justifying their use. Thermal waters from drillholes gave the same temperatures as the water temperatures in springs at all locations. Lower temperatures were obtained in deeper horizons in Mala Kladuša, Šumatac, G. Šeher, Laktaši, Tičići and Ribnica, while a drastically lower water temperature was recorded in IB-10—Ilidža at a depth of 1100 m (Miošić et al. 2013).

Table 3 Deposits with greater yields of wells compared to springs

Mineral water	Thermal water	Thermomineral water	
Mlječanica (10)*	Tržačka Raštela (4)	Gata (5)	Boljanić–Spreča (27)
Raduša–Tešanj (43)	Barake–Mala Kladuša (1)	Lješljani–B. Novi (8)	Kakanj–Bičer
Crni Vrh–Tešanj (44)	Mala Kladuša–Ilidža (2)	Vrbovac–Odžak (20)	Tičići–Kakanj (51)
Orašje Planje (41)	Donji Šumatac (3)	Ilidža–Sanski Most (14)	Radići–Kakanj (52)
Moševac–Maglaj (45)	Laktaši (15)	Gornji Šeher (17)	Vitina–Bugojno (49)
Ljubače–Mlin (37)	Kulaši–Prnjavor (19)	Slatina–Banja Luka (16)	Ilidža–Sarajevo (75)
Bokavić Ševar (36)	Spreča–Živinice (39)	Teslić (40)	Blažuj (73)
Jesenica–Zvornik (31)	Ribnica–Kakanj (53)	Bistrica–Žepče (47)	
Klokoti–Kiseljak (63)	Kraljeva Sutjeska (54)	Sočkovac (26)	
Kiseljak (67)	Olovo (58)	Gradačac (23)	
Donje Selo (81)	Fojnica (65)	Slatina–Tuzla (33)	
	Višegrad–dam of HP	Priboj (30)	
	Višegradska banja (79)	Biohan (64)	

*Number of water deposit on map

Waters with specific and rare physical and chemical properties were determined by balneologists in Lješljani, Sanska Ilidža, Kulaši, and Vajić water—Petrovo, Crni Vrh, Raduša, Srebrenica, Ilidža—Sarajevo, Biohan and Slatina—Jablanica.

Useful potentials and properties established for waters in Bosnia and Herzegovina are as follows:

- the mineral karstic permanent spring Klokun has an enormous yield Q_{min} = 2000 l/s, M = 1200 mg/L and t = 12.7 °C (Samardžić 2010),
- Toplica–Spreča is a thermal spring with maximum yield of Q = 250 l/s, t = 24 °C,
- the spring with the highest temperature (58 °C) is in Ilidža–Sarajevo with a total power of all wells of this deposit of 50 MWt,
- the highest temperature (96 °C) of an artesian well is Do-1–Domaljevac (Q = 25 l/s), at a depth of 1275 m and with a power of 9 MWt,
- artesian well GB-1—Gračanica with a depth of 68 m has an outlet temperature of 39 °C. The initial eruptive yield before casing was Q = 414 l/s, GWR = 2.5 of free 99 % pure CO_2. This aquifer located in cavernous Triassic limestone has the same temperature at the entire depth (600 m),
- in Tičići close to Kakanj, where the temperature of the spring before drilling was 28 °C, and yield Q = 2 l/s, the artesian outflow in drillhole IT-1 was Q = 35 l/s and 56 °C at a depth of only 82 m (Slišković 1993),

- Radići spring had t = 32.8 °C, Q = 0.5 l/s and the outflow in drillhole IT-2 was Q = 22 l/s and t = 39 °C,
- Fojnica well FB-2 with 150 m depth, had an artesian outflow Q = 650 l/s at the initial eruption, and after casing Q = 250 l/s, M = 233 mg/L, of the CO_2–N_2 type, water temperature t = 22.6 °C. Near FB-2 are Memića spring with the same chemistry and genesis (t = 21 °C and Q = 0.7 l/s) and subartesian wells with similar characteristics: Q = 20 l/s, M = 500 mg/L, of N_2–CO_2 type, and t = 30 °C (Slišković 1993).
- in Lješljani, well SB-1, depth 670 m, has an artesian outflow of 7 l/s, water temperature 32 °C. This hyperalkaline water has significant CH_4 concentration, which may be an indicator of hydrocarbon bearings in the ophiolitic insulator rocks (Miošić 1987a).

These data clearly show the existence of exploitable water resources in B&H at relatively shallow depths and there are the possibilities of capturing waters in deep accumulations with higher productivity and enthalpy in various geological structures.

Utilization of Waters

Archaeological remnants show the use of hydrogeotherms from Roman or even earlier times as is the case in Ilidža (2400 years BC). At present, waters are used at 47 deposits (Table 4), about 16 % of the registered total waters, but their quality, capacities and indications are inadequate. The use of mineral waters is very low, thermal higher and thermomineral waters are the most exploited.

Utilization of waters according to type and deposit is as follows:

- Salt thermomineral water near Tuzla is used by pumping salt solutions from wells as uncontrolled leaching of salt layers, salt is extracted from the solution and used as a basic raw material in the chemical industry and as common salt,
- Sulfate–arsenic–iron radioactive waters at Srebrenica have been used as a medicinal bottled water and were exported to the USA till 1914 and in balneology and therapeutics until 1992,
- Mineral waters with H_2S are used in the spa Mlječanica and in the form of primitive baths in Jelovac, and Slatina—Jablanica,
- Mineral waters with CO_2 are used for bottling in Kiseljak, Kozluk, Orašje Planje, Raduša, Bokavić Ševar, Fojničk Raskršće and a little bottling is carried out in Crni Vrh (<1 m^3/24 h). This type of water was used in Kiseljak as a therapeutic until 1992 in the former spa.
- CO_2 is extracted only in Kakmuž, and until 1992 in Klokoti and for balneological purposes there is a bath with CO_2 (spa Vrućica—Teslić),
- Radioactive thermal and thermomineral waters are used in the spas Slatina, Fojnica, Ilidža, Višegradska banja, Gata, Sanska Ilidža, Gornji Šeher, Gračanica.

Table 4 Utilization of mineral, thermal and thermomineral waters

Spa	Local and seasonal recreation	Direct heat use	Bottling	Water supply	Extraction of raw materials	Industrial use (process water)
Mineral water						
Mlječanica (10)*	Jelovac (9) Jasenica (31)		Orašje Planje (41) Crni Vrh (44) Raduša (43) Bokav. Ševar (36) Kozluk (32) Kiseljak (67) F. Raskršće (66)			Alagići (68)
Thermal water						
Laktaši (15) Kulaši (19) Dvorovi (28) Olovo (58) Višegrad (79) Fojnica (65)	Mala Kladuša (2) Spreča (39) Dvorovi (28) Višegrad (79) Fojnica (65) Toplica (71) Kreševo (70) Olovo (58) Orlja (59)	Slobomir (29) Dvorovi (28) Laktaši (15) Kulaši (19) Višegrad (79) Fojnica (65)	Mostarsko Raskršće (72)	Donji Šmatac (3) Vrbovac (20) Rudinice-Sanski Most Seljanuša (25) Mionica (24) Spreča (39) Očevlja (57) Kraljeva Sutj. (54) Kruščica (50) Jezero-Rudo		Gradačac (22)
Thermomineral water						
Gata (5) Lješljani (8) Slatina (16) Gornji Šeher (17) Gradačac (23) Sanski Most (14) Teslić (40) Ilidža (75)	Tičići (51) Lješljani (8) Sanski Most (14) Breza (56) Sočkovac (26) Breza (56)	Slatina (16) Gornji Šeher (17) Ilidža (75)	Dolac (42)		Sočkovac (26)	

*Number of water deposit on map

Modern spa facilities were built at the first five locations, while the other waters are used mainly for recreation and sport.

- Carbonated mineral water in Blažuj was bottled until 2013, and bottling in small quantities was carried out in Rječica Maglaj and Žepče.

There are 11 thermal water localities for water supplying, of which Toplica Spreča is one of the largest thermal springs in Europe (3 deposits are in the planning phase for bottling and two thermomineral waters also for bottling).

The power of hydrogeotherms used in 31 deposits is 206.3 MWt, with individual powers from 0.1 to 15 MWt, while the geothermal direct heat use is about 22 MWt which indicates a very low level of utilization of geothermal energy compared with the available capacities. As the temperature outputs from installations are far higher than 10 °C i.e. the differences of input and output temperatures of systems are very small, the real power utilization is much lower than is possible.

There are 21 spas of thermal and thermomineral waters and recreation centers with swimming pools, which are heated by geothermal waters directly or indirectly through heat exchangers and one spa of mineral waters. Thermal water is used at 6 spa and 4 sites with seasonal pools, and thermomineral water in 8 spas and 3 open pools (Table 4). Water temperatures in thermal and thermomineral spas range from 17.4 to 75 °C. The total geothermal energy used for bathing and swimming is estimated to be 83.25 TJ/year (Miošić et al. 2015).

A low capacity factor of 0.35 (Miošić et al. 2015) shows inadequate utilization of the installed capacities of hydrogeotherms. In most cases, the available capacities of waters are much higher than those needed to satisfy the actual demand; a large part of the installed capacities remaining unused over a long period each year, illustrating the possibilities for use in other purposes.

Conclusion

Bosnia and Herzegovina is rich in natural mineral, thermal and thermomineral waters of various origins, composition, concentration, locations and application in numerous water deposits. The waters are mostly renewable resources of meteoric origin with a highly-developed irregular spatial distribution and horizontal and vertical discontinuity, diversity of genesis and physical and chemical characteristics.

Most investigations were carried out up to 1992, resulting in the capture of waters by numerous drillholes and wells. Considerably greater water capacities were obtained by drilling at all deposits in relation to the springs, though it is clear that increased tapping of additional water quantities is possible by new deeper drillings in almost all active deposits. The same is true regarding any increase in the present utilization and new exploitations of waters.

The 33 geothermal waters are currently in use—19 deposits of thermal and 14 locations of thermomineral waters. The direct use of waters for geothermal energy is implemented at 21 localities. Spas and recreation centers are the main users (18 localities) and a minor proportion for individual space heating (6 locations). In respect of the mineral water, there are waters of specific physical and chemical properties which are effective for medical and balneological uses.

The level of investigation and use of waters in Bosnia and Herzegovina is less with respect to Croatia and Slovenia, and particularly to other countries of the Pannonian Basin, which implies the need for new research to study the quality and quantity of waters in more detail.

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