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ORIGINAL RESEARCH

Geochemistry and therapeutic properties of Caucasian mineral waters: a review

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Abstract The Caucasian mineral water (CMW) region is a unique area where mineral waters differ by their chemical composition and balneological properties. The presence of a wide range of mineral waters with various ions and gas components and different genesis and their therapeutic properties in the restricted area is explained by complicated geological and tectonic settings. The dominant type of mineral water in the CMW region is CO_2-bearing water with H_2SiO_3 and H_3BO_3 as the specific components. According to ion composition, gas phases' content into groundwater, total dissolved solids, and balneological characteristics, we would distinguish 9 groups and 16 types of these mineral waters, with each water type being of particular therapeutic interest. The CMW region includes four spa cities with a different therapeutic profile: Zheleznovodsk, Kislovodsk, Pyatigorsk, and Essentuki. Spa treatment is based on the use of different types of mineral waters, therapeutic muds within the region's diverse landscapes, and climatic conditions. Mineral waters are utilized in the form of baths, swimming pools, showers, various irrigations, inhalation, as well as drinking therapy. Therapeutic mineral waters are used to treat gastrointestinal problems, metabolic and nervous system disorders, as well as various diseases of liver, kidney, urinary tract, circulatory system, respiratory organs, and skin.

Keywords Mineral water · Healing water · CO_2-bearing water · Hydrochemistry · Health

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Introduction

The Caucasian mineral water (CMW) region is a unique area where various types of balneologically valuable mineral groundwater are widespread. Numerous mineral water springs, the mud Lake Tambukan, picturesque submontane landscape, an abundance of sunny days, clean air, mountain and steppe vegetation, and mild climate have created a balneotherapeutic mud mountain climatic spa. At present, the CMW region is a major resort and tourist complex with 35 thousand beds, including 90 adults and nine specialized children's sanatoriums, 16 boarding houses, four clinics of the Pyatigorsk State Research Institute of Balneology, spa clinics, balneophysiotherapeutic departments, water clinics, etc. The uniqueness of the spa area of the CMW region with four famous spa cities, such as Zheleznovodsk, Kislovodsk, Pyatigorsk, and Essentuki, is due to the exceptional diversity of types and varieties of mineral waters, the location of which is compactly concentrated in a relatively small area.

Due to highly effective balneological properties, the CMW region's mineral waters are rightfully famous not only on the Russian Federation's territory but also beyond its borders. Within the CMW area, there are CO_2-, H_2S-, CO_2-H_2S-, and radon-bearing waters, including the world-famous Essentuki #4, Essentuki #17, Narzan, as well as Smirnovskaya and Slavyanovskaya waters.

The famous saline and high pCO_2 mineral waters located in the CMW region have well-known analogs in the whole world, for example, groundwater from Saratoga Springs (the Hudson River Valley), Balaruc springs (southern France), mineral and thermal waters of Western Bohemia, etc. The famous saline and CO_2-rich cold mineral spring waters of Saratoga Springs (New York) located in the Hudson River Valley have piqued scientific interest for more than 100 years (Siegel, 1996, 2000; Back et al., 1995; Davis & Davis, 1997). The investigated mineral waters located in Europe also have continued for a long time, and at present there are a lot of scientific research studies concerning mineral springs in various European countries, for example in France (Aquilina et al., 2002), Portugal (Aires-Barros et al., 1998), Poland (Porowski et al., 2021), Croatia (Borović et al., 2016), Slovenia (Kralj & Kralj, 2000), Czech Republic (Vrba, 1996), etc.

Health resort medicine is widely used in daily clinical practice to treat skin diseases, cardiovascular diseases, osteoarthritis, and gastrointestinal disorders in many European countries (Grassi et al., 2002; Petraccia et al., 2006; Quattrini et al., 2016; Stier-Jarmer et al., 2015). Healing of a wide range of diseases occurs at spas in the CMW region (Efimenko, 2015; Efimenko & Fedorova, 2013; Soprun & Reps, 2013). Spa treatment is based on the use of different types of mineral waters, therapeutic muds, and landscape and climatic conditions of the region (Uiba et al., 2016).

The dominant type of mineral water in the CMW region is CO_2-rich water, featuring various ion salt and gas compositions, TDS, and balneological characteristics (Filimonova et al., 2020). CO_2-rich mineral water is used in the complex treatment of many diseases both for external (general and local baths, showers, bathing, and swimming in pools with mineral water) and for internal applications (drinking, stomach, intestines, microclusters, etc.), as well as inhalations. The therapeutic effect of mineral water on health is determined by several factors: ionic composition of water and components that give water-specific properties (gases, biologically active substances, organic substances), temperature, and pH.

The CMW region has a 200-year history of geological investigation. Yet, much fundamental knowledge about hydrogeochemistry, circulation paths, and origin of the most therapeutically valuable CO_2- and H_2S-bearing waters is still missing. The reason is significantly complicated by the geological and tectonic structure of the territory and its hydrogeodynamic and hydrogeochemical conditions.

At the present time, there is no generally accepted concept explaining the genesis of mineral waters of the Mineralovodsky artesian basin and the input mechanisms for ion salt, isotopic, and gas compositions. The primary goal of this article is to review the main types of mineral waters of the region, to present detailed information about (1) the history and classification of mineral water in the Russian Federation, (2) the geological and hydrogeological settings of the Caucasian mineral water region, (3) the main aspects of the chemical composition of Caucasian mineral groundwater, and (4) the therapeutic properties of Caucasian mineral water. Notably, in this paper, we will not review the conditions of mineral water origin.

Classification of mineral water in Russian Federation

Water demand and its application is continuing for centuries in all countries. Groundwater can be divided into groups based on the designated use: water suitable for drinking (fresh or table water); water suitable for technical or industrial purposes (miscellaneous use water); mineral water (medical or therapeutical); and water from which some useful components can be mined (brines, usually). One of the first definitions of mineral water was given by Ovchinnikov (1947): Mineral water is water with TDS of more than 1 g/dm^3, having a therapeutic effect on human health due to an increased content of useful, biologically active components of the chemical and gas content, or typical chemical composition, or organic substances. This definition was further developed by Nevraev and Ivanov (1964): They referred to mineral waters as natural waters containing increased concentrations of some or other mineral, organic components and gases and (or) possessing some physical properties, due to which these waters have a therapeutic effect on the human body, different from the action of freshwater. In Russian National State Standard (NSS R 54,316—2011), biologically active components (boron, bromine, arsenic, total iron, iodine, silica, organic compounds, free carbon dioxide) are listed (National State Standard, 2011).

A variety of chemical compositions of mineral waters and their physical properties led to numerous classifications of these waters, based on the TDS, temperature, chemical or gas composition, biological activity, and application of mineral waters. According to Russian National State Standard (National State Standard, 2011), the curative drinking waters by TDS value are divided into five groups: from freshwater (< 1 g/L) to rich mineral content water (10–15 g/L) (Table 1). Mineral water with TDS higher than 15 g/L can only be used externally: for bath, basin, shower, etc.

By temperature, mineral waters may be cold (< 20 °C), hypothermal (20–37 °C), thermal waters (37–42 °C), and hyperthermal waters (> 42 °C). According to the prevailed gas phase, there are nitrogen, carbon dioxide, methane, and radon mineral waters. By radioactivity, mineral waters are classified as very weak radon waters (185–750 Bq/L), weak radon waters (750–1500 Bq/L), medium radon waters (1500–7500 Bq/L), and high radon waters with radon activity above 7500 Bq/L. Ivanov and Nevraev originally developed the water classification in 1964 (Ivanov & Nevraev, 1964), and it is widely used in Russia and other European countries. This classification is based on the main balneological components: free carbon dioxide, total iron, boron, bromine, arsenic, iodine, silicon, and organic compounds. The actual National Russian Standard of biologically active components in mineral waters is presented in Table 2.

According to predominant ionic composition, mineral waters are divided into hydrocarbonate (bicarbonate), sulfate, salt, or sulfurous waters. In the case where two anions predominate, the waters can be hydrocarbonate–sulfate, salty–sulfate, or chloride–hydrocarbonate. Current Russian classification, accepted in NSS R 54,316—2011, is based on predominant chemical elements (anions and cations) with biologically active components.

In the international scientific literature, the European Union (EU) Directive is often used to classify natural mineral water. However, local standards differ per country. In accordance with European legislation (2009/54/EC Directive), natural mineral water is defined as microbiologically wholesome water from an aquifer tapped via one or more natural or drilled wells and has specific hygienic features and, eventually, healthy properties (Monique, 2003). The criteria for the chemical composition of natural mineral water in accordance with the EU natural mineral water directives are given in Table 3. These criteria show a distinction based on TDS and a further specification based on some characterizing cations and anions or carbon dioxide content. Chemical composition of natural mineral waters is classified according to

Table 1 Classification of mineral drinking water by TDS (National State Standard, 2011)

Type of water	TDS, g/L	Application
Freshwater	< 1	Table water, healing–table water*, healing water*
Very low mineral content water	1–2	Healing water*
Low mineral content water	2–5	
Medium mineral content water	5–10	
Rich mineral content water	10–15	Healing water

*if biologically active components are present in mineral water

Table 2 Balneological standards of biologically active components in mineral waters (National State Standard, 2011)

Mineral water group	Biologically active component	The value of mass concentration The biologically active component, mg/L	
		Healing water	Healing–table water
CO_2 rich	CO_2(aq)	–	> 500
Iron rich	Fe	–	> 10.0
Arsenic rich	As	> 0.7	–
Boron rich	B	> 60.0	35.0–60.0
Silica rich	Si	–	> 50.0
Bromine rich	Br	> 25.0	–
Iodine rich	I	> 10.0	5.0–10.0
Organic rich	Organic compounds	> 15.0	5.0–15.0

Table 3 Criteria for natural mineral waters in accordance with the EU natural mineral water directive (Monique, 2003)

Natural mineral water type	Criterion
Very low mineral concentration	Mineral content (TDS) < 50 mg/L
Low mineral concentration	TDS 50—500 mg/L
Intermediate mineral concentration	TDS 500—1500 mg/L
High mineral concentration	TDS > 1500 mg/L
Containing bicarbonate	Bicarbonate > 600 mg/L
Containing sulfate	Sulfate > 200 mg/L
Containing chloride	Chloride > 200 mg/L
Containing calcium	Calcium > 150 mg/L
Containing magnesium	Magnesium > 50 mg/L
Containing fluoride	Fluoride > 1 mg/L
Containing iron	Bivalent iron > 1 mg/L
Acid	Carbon dioxide dissolved > 250 mg/L
Containing sodium	Sodium > 200 mg/L
Suitable for low-sodium diets	Sodium < 20 mg/L

prevail ion as bicarbonate, sulfate, chloride, sodium-rich, calcium-rich, magnesium-rich, fluoride-rich, and ferrous mineral waters.

Natural mineral waters are also classified by other physical parameters, like pH, temperature and hardness. With regard to pH, natural mineral waters are classified as acid water (pH < 7) or alkaline water (pH > 7). Hardness indicates the presence of alkaline earth metals, and natural mineral waters may be very soft (0–100 mg/L of $CaCO_3$), soft (100–200 mg/L of $CaCO_3$), hard (200–300 mg/L of $CaCO_3$), or very hard (> 300 mg/L of $CaCO_3$). Finally, classification can be based on biological activity. Thus, there are diuretic mineral, cathartic, reconstituent waters, or waters with antiphlogistic and resolvent properties (Albertini et al., 2007; Petraccia et al., 2006).

Mineral water makes a significant contribution to human health, but the amount of water consumed may vary from person to person. The choice of the water to drink can be variable, and it depends on the personal necessity. Mineral waters differ from drinking water due to their spring purity and conservation, the constant level of minerals (trace elements or other constituents), and, where appropriate, for certain effects they can determine. For example, gastrointestinal system results to be stimulated by natural mineral waters. In particular, bicarbonate and chloride mineral waters proved to have positive effects for gastric function. Chloride mineral waters are mainly used for hydroponic therapy, stimulating gastric emptying and gastro-duodenal peristalsis. Bowel function results to be promoted by sulfate and magnesium mineral waters, in terms of reduction in constipation, improvement in the constipation symptoms, and overall bowel movements. In iron deficiency anemia and in the treatment of anemia for pregnant woman, ferrous waters are highly recommended. Calcium-rich mineral waters increase bone mineralization, considering both femoral and spinal bone mineral density after calcic waters intake (Quattrini et al, 2016).

Fluoride-rich mineral waters may be indicated for children, because they can reduce the incidence of decay and promote bone mineralization. However, the consumption of mineral water with high F^{-} content has to be maintained low because fluoride-rich mineral water active utilization may have some toxic effects: from dental fluorosis to skeletal fluorosis, if fluoride intake is above 10 mg/L (Albu et al., 1997; Quattrini et al., 2016). For this reason, the European Food Safety Agency (EFSA) established fluoride upper limit of exposure to 1.5 mg/L. This value limit is confirmed also by World Health Organization.

The therapeutic use of mineral water as a drink, in accordance with the uses prescribed subsequent to a medical visit, is one of the most important forms of health treatment.

History of investigation of the Caucasian mineral water

Investigation of mineral water in Russia began with Peter the Great. Thus, a special contribution to the study of mineral springs was made by the Russian Academy of Sciences, founded by Peter the Great in 1724. The first ferrous water spas were opened in Karelia and Lipetsk then. A significant event was discovering the Caucasian mineral waters region (CMW region), the hydrogeologically unique area with almost all known CO_2-rich groundwater types. In the 200-year history of geological investigation of the CMW region, five significant periods can be identified:

- I period: from the beginning of the eighteenth century to the beginning of the twentieth century;
- II period: 1906–1941;
- III period: 1945–1985;
- IV period: 1986–2003;
- V period: from 2004.

In the I period, the scattered study of mineral water sources was performed, and exploration of the region began: The main types of mineral groundwater in Kislovodsk, Essentuki, Pyatigorsk, and Zheleznovodsk were discovered and described, several mineral springs were taped, and therapeutic muds have been investigated. The first mention of the Narzan mineral spring, located in Kislovodsk, appeared in the Academy of Sciences reports in 1760; its scientific description dates back to 1793 by P.S. Pallas. The detailed description of the spring, its composition, and curative properties was left by the famous researchers of the CMW region, such as Gaas (1811), Nelyubin (1825), and Batalin (1861). Engineers A.I. Nezlobinsky and K.F. Rugevich have created a hitherto extant spring capturing. Pyatigorsk mineral springs were first examined and briefly described in 1773 by I. A. Guldenstedt. In 1793, P. S. Pallas concluded the high curative properties of the Pyatigorsk thermal waters (Glukhov, 2013). By the time of the official opening of the spa in 1803, hot springs had been quite thoroughly examined by several researchers, mainly in physical and chemical and partly in therapeutic respects. The first documents about springs in Essentuki and Zheleznovodsk were dated by 1810, mentioned by doctor F.P. Gaas (Ivanov, 1972). Due to the low discharge rates of Essentuki springs, F.P. Gaas was not interested in them but paid great attention to Zheleznovodsk springs with high temperature and dissolved ferrum. This spring was called No. 1—one exists in the reconstructed form to the present day.

In the nineteenth century, many researchers took part in discovering CO_2-rich mineral springs around mountain iron (Zheleznaya). In honor of the first investigators of the Zheleznovodsk groundwater basin, many springs were named Gansovsky, Francois, Smirnovsky, and Nezlobinsky. Professor A.P. Nelyubin identified the medical significance of saline groundwater in Essentuki in 1823 (Potapov & Danilov, 2012). He described 28 springs and the springs # 4 and # 17, well known as trademarks “Essentuki-4” and “Essentuki-17.” The development of Essentuki resort was hampered by low flow rates of mineral springs, despite the high therapeutic properties of water. The genesis of mineral waters was first considered by Batalin (1861), Abih (1874), and Nezlobinsky (1895). In 1899, the first congress of balneologists of Russia was held (Voronov, 2000). By this time, in Russia, there were more than 30 mineral water spas.

The beginning of the twentieth century (II period) was characterized by organized and focused searching and exploration works under the guidance of A. N. Ogilvy, J.V. Langwagen, H. N. Slavyanov, and other famous scientists. During this period, exploitation and observed wells were drilled, new springs were captured, and overage constructions were rebuilt. New types of mineral water, such as Warm Narzan (Pyatigorsk), Slavyanovsky (Zheleznovodsk), Dolomite Narzan, and Sulfate Narzan (Kislovodsk), were discovered. During the same period of time, the supplies of "Essentuki-4" and "Essentuki-17" were significantly enlarged. By drilling and experimental works, J.V. Langwagen concluded the deep origin of mineral waters. He concluded that deep groundwater rises along the cracks from great depths of Earth crust, and then it gets diluted with shallow freshwater of upper Cretaceous limestone. In 1914, A.N. Ogilvi published "To the question of the genesis of Essentuki spring." The author evaluated the reasons for the chemical composition diversity of saline–alkaline waters and confirmed previous researchers' conclusion regarding the mixing between the deep mineral groundwater stream and shallow freshwater.

The extensive investigation of the CMW region began after World War II (period III). To meet the mineral water demand of the fast-growing number of resorts, new mineral groundwater areas were discovered and explored. Major complex studies were carried out together with the fieldwork that allowed to understand the main features of geological and hydrogeological settings of the CMW region and estimate the supply of mineral groundwater. During this period, several principal theories explaining the genesis of prevailed mineral water types were suggested. The experimental studies of Shinkarenko (1946) suggested that the process of deep metamorphism in sediments is involved in the formation of the chemical composition of mineral water. Panteleev (1963) proposed that Essentuki mineral groundwater is formed by mixing of three aquifers: thermal CO_2-rich Titon–Valanginian aquifer, fresh Apt-Albian aquifer, and Cl–Na waters with high TDS circulated within the upper Cretaceous limestone. Then, this mixture is being transformed by the cation exchange, biogenic sulfate reduction, and other processes. Similar processes occurred for saline–alkaline groundwater in a different area in the CMW region (Ivanov, 1972). While analyzing the extensive material of the Caucasian region in 1985, S.A. Shagoyants concluded that the CO_2-rich mineral water "Essentuki-17" is formed in the south of the CMW region. Then, groundwater flows up along the aquifer, uprising from the north to the south, and reaches the Essentuki field. Criteria for evaluation of curative mineral waters were developed by Ivanov and Nevraev (1964).

From the end of the twentieth century to the beginning of the twenty-first century (IV period), many field and cameral works and detailed studies were carried out mainly by local organizations from the CMW region. In 1992, the CMW region was given the status of a Specially Protected Ecological and Resort Area (SPA) of the Russian Federation. The result of many years of purposeful research was a regional characterization of current hydrogeological conditions in the CMW region on the scale of 1:200 000. JSC "Kavkazhydrogeologiya" and JSC "GIDEK" assessed mineral and fresh groundwater's resource potential in the CMW region. They proposed that the mineral water resources' main component is a gas–liquid fluid from the crystalline foundation.

In recent years (V period), mineral resources study has been mainly based on previous data and ongoing surveys, computer modeling, and isotope chemical results (Filimonova et al., 2020; Lavrushin, 2012; Lavrushin et al., 2020). Due to the complexity of geological and tectonic structure and hydrogeological conditions of this region, there are still no generally accepted concepts of the formation of groundwater reserves and chemical composition. Based on the entire history of mineral water study, there are two predominating ideas of mineral water formation:

(1) The saline–alkaline groundwater originates in the basement (near Titon-Valanchine sediments). It then migrates through the tectonic "windows" or "discharge pipes" along the Gothiev-Aptian rocks (up to 700 m thickness) directly to the upper Cretaceous and Paleocene carbonate rocks. That is where water gets enriched with CO_2 gases. According to this idea, the gas phase is preferably mantle (Ostrovskiy, Abramov).

(2) CO_2-rich saline–alkaline groundwater is meteoric groundwater and recharge area located between the North Caucasian monocline and Stavropol Rise (Panteleev, Shagoyants, Potapov). This water gets enriched by different chemical components during leaching from Lower Cretaceous–Paleocene sediments. Then, water moves throughout tectonic faults in Upper Cretaceous–Paleocene rocks, and the layers uprising from north to south.

Recently, Lavrushin et al. (2020) suggested a new hypothesis that Essentuki saline–alkaline groundwater may have a "relict" (or sedimentogenic) origin. According to this idea, these waters were circulating in all the aquifers of the CMW region before the Pliocene phase of volcanic activity in this region. Later, this groundwater was almost everywhere diluted or replaced by infiltration water flow from the Greater Caucasus's mountain structure. Today, those mineral waters have survived only within the Upper Cretaceous aquifer. One of the factors contributing to the preservation of these waters here is the reverse regime of groundwater movement in the south direction, which prevents the infiltration of water flow into this complex (Lavrushin et al., 2020).

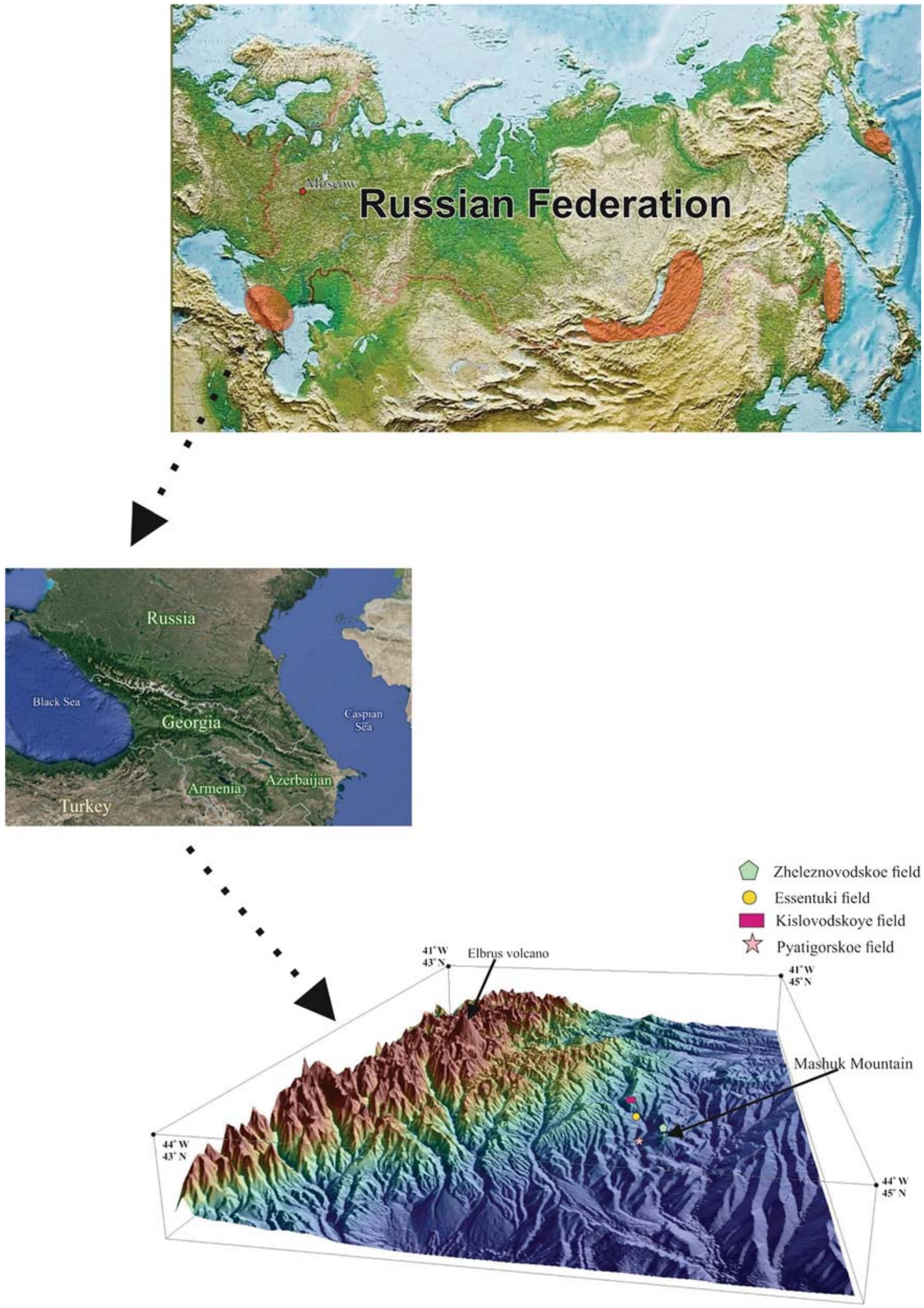
Geology and hydrogeology of the CMW region

The CMW region is located in the south of the European part of Russia, right between the Black and Caspian Seas, on bonding the Mineralovodskaya plain and the northern slopes of the Greater Caucasus. The region's area is 5243 sq. km, including resort cities: Mineralnye Vody, Zheleznovodsk, Kislovodsk, and others. The CMW region is located only 90 km from the highest mountain in Europe—Elbrus (Fig. 1). The region's relief is divided into the mountainous southwestern part (2000–2400 m a.s.l.) and the almost flat northeastern part (400–800 m a.s.l.). In addition to the cuesta forms, 17 volcanic mountains give it a unique character to the CMW area's relief. The mutual position of these peaks shows certain northeastern linearity toward Elbrus. Such a linear location of volcanic mountains is explained by the magmotectonic structure of the northern Elbrus region. Surrounded by the largest laccolite Beshtau (1440 m a.s.l.), there are volcanic mountains: to the north—Zmejka (994 m a.s.l.), Zheleznaya (951 m a.s.l.), Razvalka (930 m a.s.l.), Kinzhal (567 m a.s.l.), and Kokurtly (403 m a.s.l.); to the west—Sheludivaya (874 m a.s.l.), Ostraya (881 m a.s.l.), Tupaya (772 m a.s.l.), and Medovaya (721 m a.s.l.); to the northwest—Byk (821 m a.s.l.) and Verblud (902 m a.s.l.); to the southeast—Mashuk (999.3 m a.s.l.) and Zolotoy Kurgan (828 m a.s.l.); and to the south—Yutsa (912 m a.s.l.) and Dzhutsa (1125 m a.s.l.) (Fig. 2). The laccolite peaks disturb the monocline structure of the Neogene, Paleogene, and the underlying Cretaceous rocks (Filimonova et al., 2020).

The river network of the CMW region belongs to the Caspian Sea basin. Thus, the main river is the Kuma River and its tributaries Podkumok, Surkul River, and others. The Kislovodsk, Essentuki, and Pyatigorsk are located in the Podkumok River valley, while Zheleznovodsk is in the Kuma River valley. Locally well-known Tambukan and Lysogorsk lakes contain bitter saline water and present a valuable source of therapeutic mud.

The climate of the CMW region is kindly and varies greatly. Such atmosphere is formed under the influence of natural factors: southern latitudes of the area, its location between two seas, and its proximity to subtropical and steppe climates. The local factors include submontane location, the Great Caucasus Range's proximity, as well as arid steppes and semideserts of the northern Caspian Sea area. According to climatic conditions, the CMW region can be divided into two zones: the southern zone of Kislovodsk with features of the low mountains continental climate and the northern area of Essentuki, Pyatigorsk, and Zheleznovodsk with typical features of the steppe zone. The climate is one of the essential facilities for resort healing. For example, the low-mountain helical climate of Kislovodsk (with 327 sunny days per year) is used for therapy of cardiovascular, neurological, and respiratory diseases, including bronchial asthma. Research conducted by scientists from the State Research Institute of Balneology has shown that sun exposure and climatotherapy can delay the development of hypertension and atherosclerosis (Grigoriev & Chernetsov, 2010).

The Caucasian Mineral Water region's geological structure and its hydrogeological conditions are incredibly complicated and unique (Figs. 2, 3). This is determined primarily by the region's location in the northern part of the Greater Caucasus mega-


Moscow
Russian Federation
Russia
Black Sea
Georgia
Caspian Sea
Armenia
Azerbaijan
Turkey
Zheleznovodskoe field
Essentuki field
Kislovodskoye field
Pyatigorskoe field
41° W 43° N
Elbrus volcano
41° W 45° N
Mashuk Mountain
44° W 43° N
44° W 45° N

◀**Fig. 1** Location of the study area

anticlinorium on the joint with the Scythian (Pre-Caucasian) epi-Hercynian plate. The geological and tectonic aspects of the region are the following:

(1) The geological feature consists of a two-stage structure: basal complex and carbonate–terrigenous sedimentary cover with a total thickness of 1500–1800 m, declined in the northeastern direction. The increase in the depth of layers and distance from the recharge area causes consequently changes in the chemical and gas composition of mineral water.
(2) Significant stratum of Neogene clays overlays Palaeogenic and Upper Cretaceous carbonate sediments, conserving high-salinity groundwater. In the monocline's southern part, a subjacent Lower Cretaceous aquifer appears on the surface without overlaying sediments and recharges by precipitation. Frequently, fresh flow causes stepwise freshening in lateral migration in the northeastern direction.
(3) The region is fractured by a large regional faults system in the northeast and northwest direction, reaching the crystal foundation. The faults and the surrounding fractured rocks serve as vertical channels for fluid migration between layers, from basal complex to sedimentary cover, and as lateral channels that speed migration inside aquifers.
(4) Magmatic granitic laccolite peaks create thermal, hydrochemical, and gaseous anomalies and generate CO_2.

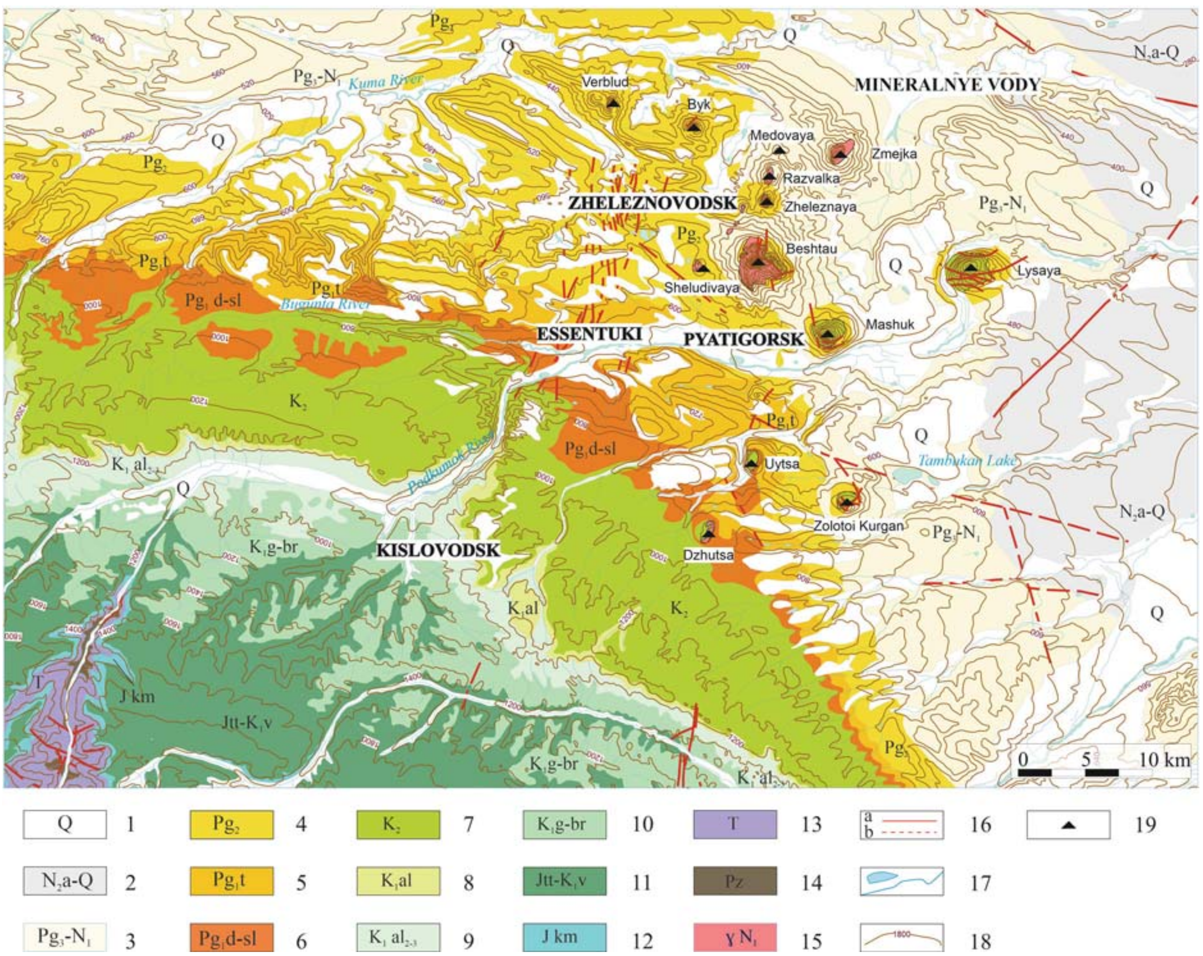


Fig. 2 Geological map of the study area

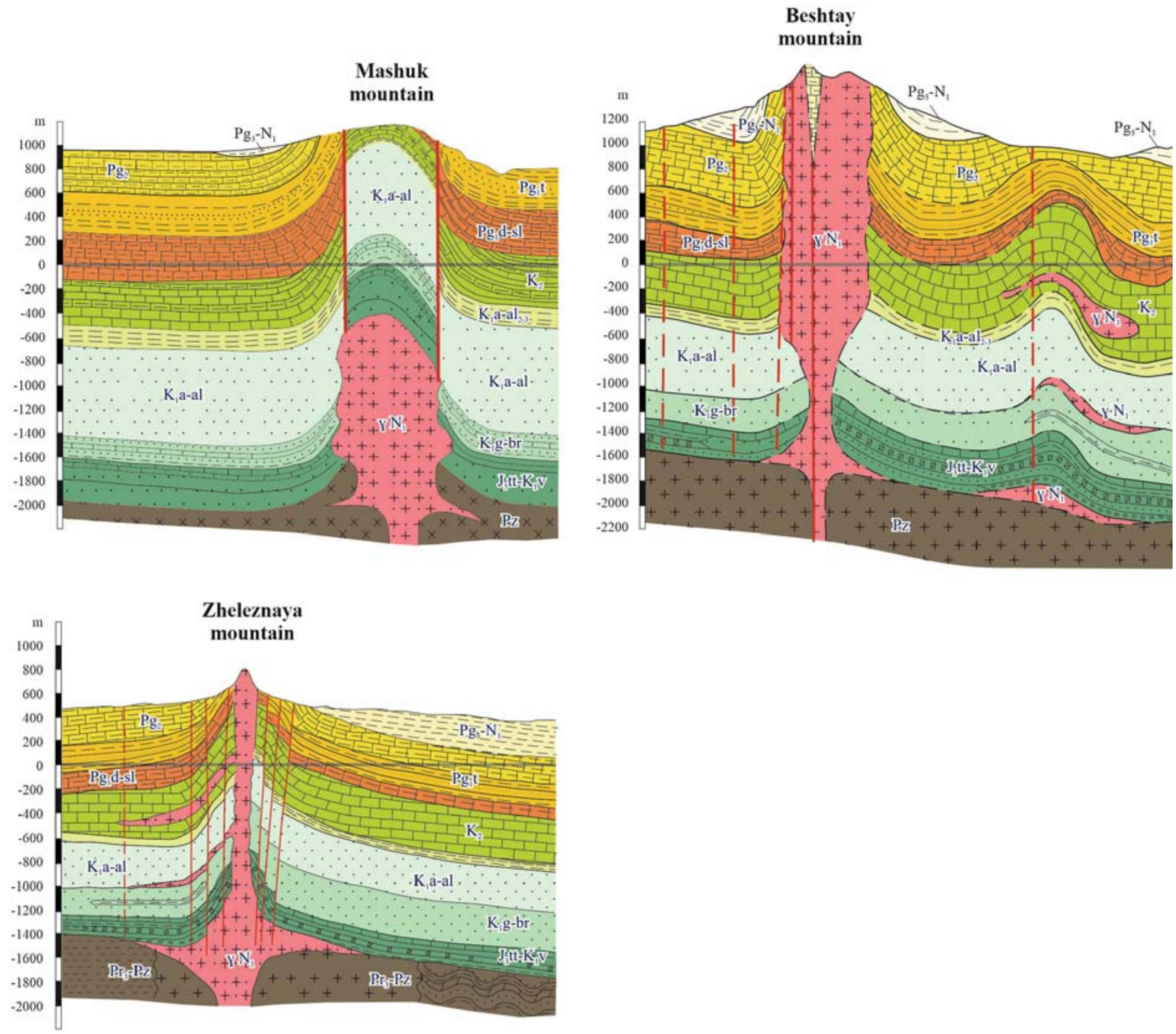


Fig. 3 Representative geological sections via the laccoliths. Legend is shown in captions of Fig. 2

The spatial distribution of aquifers and aquitards and description of their lithological composition are shown in Fig. 2. The major aquifers of the CMS region, from which mineral groundwater is extracted, are the following:

- The Danish–Zealand aquifer (Pg_1d-sl).
- The Upper Cretaceous aquifer (K_2).

1—The Quaternary aquifer. Round stones, gravel, pebble sediments, sands, sandy loam, clays; 2—The Neogene–Quaternary alluvial aquifer. Pebble sediments, sands, clays; 3—The Oligocene–Miocene (Maikop) aquitard. Clays with interlayers of sand, siltstones, sandstones, siderites, marl; 4—Eocene aquitard. Marls, limestone clays, layers of limestone, and sandstone; 5—Taneta aquitard. Clays, sands, sandstones; 6—Danish–Zealand (Elburg) aquifer. Marl, limestone, clay interlayers, siltstones, sandstones, gravelites; 7—Upper Cretaceous aquifer. Limestone, marl, bundles of sandstone in the roof and base; 8—Mid-Upper Albanian aquitard. Clays, argillites, interlayers of siltstones, sandstones, gravelites; 9—The Aptian–Lower Albanian aquifer. Sandstones and siltstones with interlayers and clay bundles; 10—The Gotteriv–Baremsk local aquifer. Interchange of sandstones, siltstones and argillites, layers of limestone, gravelites, and conglomerates; 11—The Titon–Valanginian aquifer. Limestone, lime breccia, marl, granite wood, red-colored clays, interlayers and packs of sandstone, siltstones, gravelites, gypsum, and anhydrite; 12—The Cimmerian aquifer. Limestone, sandstone, dolomite, lime breccia and gypsum in the roof, conglomerates in the base; 13—The Triassic aquifer. Interchange of sandstones, siltstones and argillites gravelites and conglomerates, layers of coal, coal shale; 14—Proterozoic crystalline basement rocks. Granites, quartz diorites, granodiorites, hyperbasites, serpentinites, slates, sandstones, siltstones, phyllites, limestones; 15—The Neogene intrusions of granites, diorites and granodiorites; 16—Faults, a: defined, b: expected; 17—river, lake; 18—hypsometric curve; 19—mountain peak.

- The Lower Cretaceous aquifer (K_1a-al$_1$).
- The Titon–Valanginian aquifer (J_3tt-K_1v).

The detailed hydrogeological description of principal aquifers is presented in Lavrushin (2012) and Filimonova et al. (2020).

The chemical composition and types of mineral waters of the CMW region are represented on hydrochemical maps (Fig. 4). The hydrochemical map shows the water type for each aquifer in different colors, as well as TDS isolines. In order to create this map, we used chemical groundwater type; the ion was included into consideration if was more than 20% meq/L. The blue sector is the area with predominant HCO_3^- groundwater type, the yellow sector—sulfate water type, and the red sector—chloride water type. The sectors with stripes are drawn in case of circulating water with two main anions; if approximately equal proportions of three anions were fixed, the color dots are added.

Geochemistry of Caucasian mineral waters

The Caucasian mineral water region is a unique place. Numerous mineral water types with different chemical compositions are concentrated in a relatively small area, which has an essential balneological significance (Table 3, Figs. 4, 5). The variety of mineral water types can be explained by the region's geological structure, such as the area's tectonics, the rock's lithological composition, the intensity of post-volcanic processes, and other geomorphological features (Filimonova et al., 2020). Within the study area, 9 groups and 16 types of CO_2-bearing waters can be identified by their ion salt, gas composition, TDS, and balneological properties, divided by their use into healing–table and table mineral waters (Table 4). Mineral waters are carbon dioxide by gas composition. H_2SiO_3 and H_3BO_3 are present among the specific components. Most of them refer to healing–table carbon dioxide mineral waters. Each of these types of water is of particular therapeutic interest. The characteristics of the four main types of mineral waters and their distribution in the area are given below.

Zheleznovodsky type of mineral waters

Zheleznovodsk mineral waters field is located in the central part of the Caucasian mineral waters region, on the slopes of Zheleznaya mountain. The typical Zheleznovodsky's mineral waters are *Smirnovskaya* and *Slavyanovskaya* brand name. This groundwater belongs to the **Na-Ca-HCO_3-SO_4** water type (Fig. 5) and differs only in temperature (Table 4). Both waters are confined to Paleogene (Pg_1d-sl) and Upper Cretaceous (K_2) sediments, and they are found in a depth range of 74 to 293 m (Fig. 4). TDS of Zheleznovodsky's mineral waters is 3.0–4.0 g/L; CO_2(aq) is 0.5–1.0 g/L; and pH is 6.2–6.7. *Slavyanovskaya* thermal mineral water has a high temperature at about 55 °C, although *Smirnovskaya* is colder with temperature ranges from 20 to 40 °C. The solute phase is dominated by salts: $Ca(HCO_3)_2$—32%, Na_2SO_4—37%, and NaCl—17%. *Slavyanovskaya* healing–table mineral water is widely known for its beneficial effect on the functional state of the gastrointestinal tract, liver, and kidney tract.

Kislovodsky type of mineral waters

Kislovodsk mineral waters field is located in the southwestern part of the Caucasian mineral waters region. Typical representatives of the Kislovodsk type of mineral waters are *CO_2-bearing groundwater—Narzan (Dolomite Narzan and Sulfate Narzan) brand names* which belong to **Ca-Mg-Na (Ca-Mg, Ca-Na-Mg) HCO_3-SO_4** water types (Fig. 5). These waters are found in a depth range of 55 to 509 m in the dolomized limestones (K_1v) and underlying sandstones (J_3tt) (Fig. 4, Fig. 5).

TDS of these waters varies between 2.0 and 3.0 g/L; CO_2(aq) concentration is 1.0–2.5 g/L; pH is 6.3; and water temperature is 13–15 °C. Alkaline earth

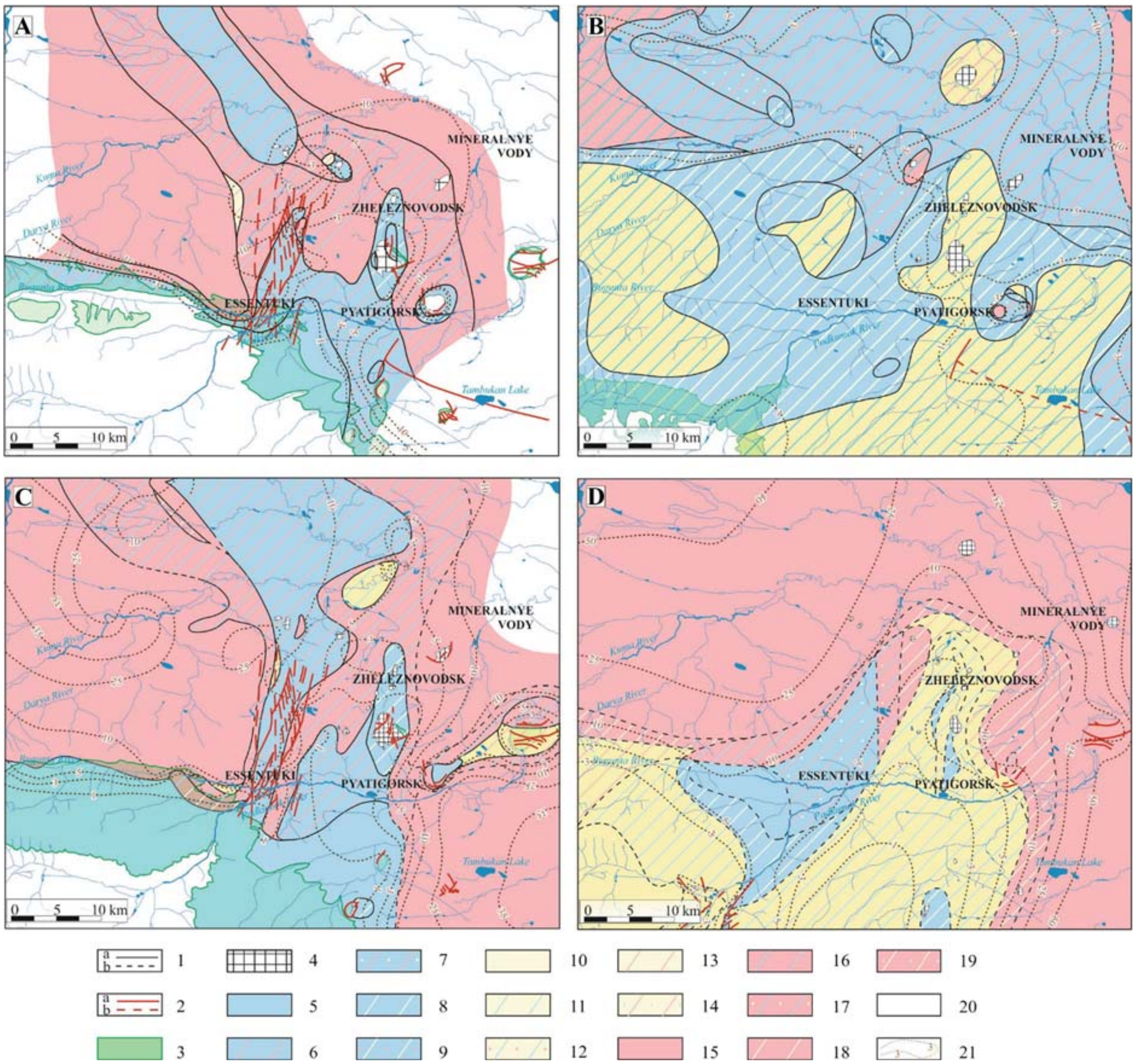


Fig. 4 Simplified hydrochemical maps of aquifers and well locations within the CMW region (compiled from Timokhin, 2006). **A**—the Danish–Zealand aquifer (Pg_1d-sl), **B**—the Upper Cretaceous aquifer (K_2), **C**—the Lower Cretaceous aquifer (K_1a-al_1), D—the Titon–Valanginian aquifer (J_3tt-K_1v). Numbers: 1—zone boundaries (a: established, b: alleged), 2—faults (a: established, b: alleged), 3—outlets under Quaternary sediments, 4—dry zones near laccoliths. Spreading area of groundwater according to prevailed ion content: 5—HCO_3 type, 6—HCO_3–SO_4 type, 7—HCO_3–SO_4–Cl type, 8—HCO_3–Cl type, 9—HCO_3–Cl–SO_4 type, 10—SO_4 type, 11—SO_4–HCO_3 type, 12—SO_4–HCO_3–Cl type, 13—SO_4–Cl type, 14—SO_4–Cl– HCO_3 type, 15—Cl type, 16—Cl–HCO_3 type, 17—Cl–HCO_3–SO_4 type, 18—Cl–SO_4 type, 19—Cl–SO_4–HCO_3 type, 20—no data, 21—TDS lines (in g/L)

components predominate among cations. Salts dominate in the dissolved phase: $Ca(HCO_3)_2$—60%, $MgSO_4$—23%, and Na_2SO_4—6%.

The hydrocarbonate ion source is dolomitized limestone; sulfate genesis is associated with the desalination of gypsum from sediments (J_3tt); and CO_2 is of volcanogenic origin (along the zones of tectonic faults).

Narzan is mineral water with unique therapeutic properties. It has high medicinal qualities, and it is used for balneotherapy and as table water. It helps to

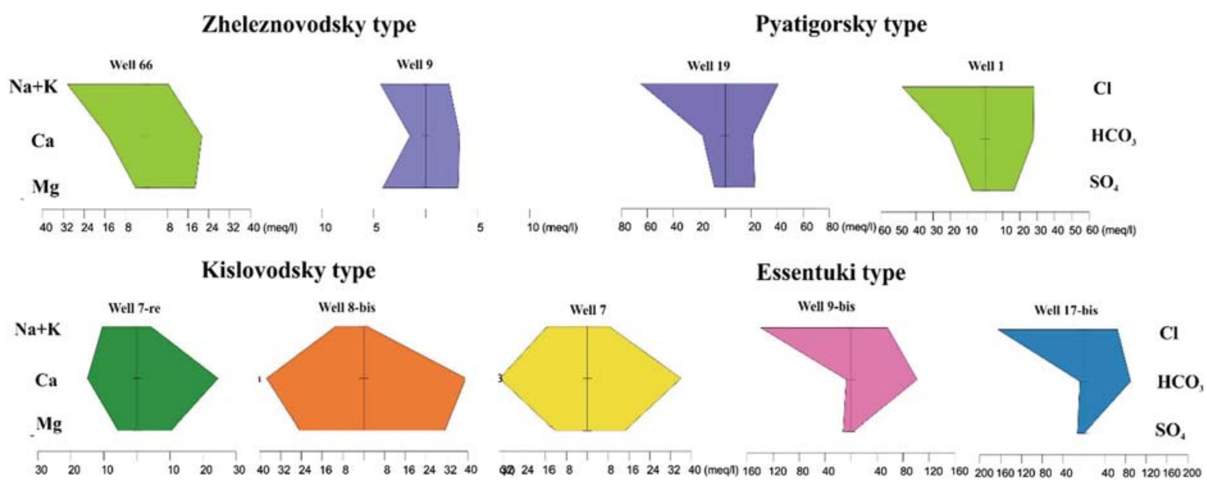


Fig. 5 Stiff diagrams for different types of natural mineral groundwater circulated within the CMW region

cope with respiratory and digestive tract diseases and normalizes the body's metabolic processes.

Pyatigorsky type of mineral waters

Pyatigorsk mineral waters field is located in the central part of the Caucasian mineral waters region, on the slopes of Mashuk mountain. One of the well-known representatives of Pyatigorsky type of mineral waters is CO_2-rich healing drinking water enriched of silica (as H_2SiO_3 component up to 70 mg/L) and registered as Mashuk #1 trade label that belongs to Na (Na-Ca) Cl-HCO_3-SO_4 type (Fig. 5).

Mashuk #1 mineral waters are confined to the Upper Cretaceous ($\breve{K}_2$) and Danish–Zealand horizons (Pg_1d-sl), revealed in the interval of 82.32–201.0 m.

TDS of these mineral waters put in the range 4.0–5.5 g/L and CO_2(aq) can reach 2.0 g/L. H_2SiO_3 is a balneological component in this water with content 0.05–0.07 g/L. According to outlet temperature (at about 27 °C) this water is hypothermal. The following salts dominate in the dissolved matter: The main is NaCl (36%), the second is $Ca(HCO_3)_2$—34%, and the third is Na_2SO_4—23%.

It is known that the practical use of Mashuk springs began much earlier than 1773 years, and at present, this type of water is recommended to utilize for chronic illnesses of the digestive organs, gastritis, liver diseases, chronic diseases of the urinary tract, and metabolism disorders.

Essentuki type of mineral waters

Essentuki mineral waters field is located in the central part of the Caucasian mineral waters region. The most well-known representatives of Essentuki type of mineral waters are high pCO_2 waters named as *Essentuki #4* and *Essentuki #17* trade mark. These waters belong to **Na-HCO_3-Cl (Cl-HCO_3)** water type (Fig. 5) and have enrichment with H_3BO_3 (Table 4). Individual attribute of the water is an approximately equal content of hydrocarbonate and chloride ions. The content of main ions in the *Essentuki #4* and *Essentuki #17* is practically identical; however, TDS differs remarkably (almost 4 g/L). These waters are confined to Paleogene (Pg_1d-sl) and Upper Cretaceous ($\breve{K}_2$) sediments (Fig. 4), and they are found in a wide depth range (from 92.4 to 998.9 m).

TDS of Essentuki #4 ranges from 7.0 to 10.0 g/L, and pH value ranges from 6.2 to 7.7. The temperature of the outlet is limited by the well depth and ranged from 14 to 53 °C. The main balneological components are CO_2(aq), which can reach 1.8 g/L, and H_3BO_3 with values 0.03–0.06 g/L.

TDS of *Essentuki #17* is higher than in Essentuki #4 and put in the area 10.0–14.0 g/L. pH values depend on the well and vary from 6.3 to 8.4. The outlet temperature depends on the subsurface water circulation depth and ranges from 14 to 38 °C. Therapeutic components in this water are CO_2(aq) reaching 2.4 g/L and H_3BO_3 with content 0.04–0.09 g/L.

Essentuki type of mineral waters has long been used in balneology and for bottling as healing–table waters.

Table 4 Types of mineral waters, distributed in the CMW region, by Russian National Standard further supplemented (National State Standard, 2011)

Nº	Well number	Mineral water group	Hydrogeochemical type of mineral water	Name of mineral water	TDS, g/L	T°C	Main ions, % meq/L	Balneological component, mg/L	Water use
1	70	Na-HCO_3	Essentuki Gorny	Essentuki Gornaya	0.5–0.8	11.0–16.0	HCO_3 60–85, (Na + K) > 80	–	Table
	26-n, 43		Nagutsky 26	Nagutskaya 26	4.0–7.0	61.0	HCO_3 > 70, (Na + K) > 90	CO_2(aq) 500–800	Healing–table
	56		Nagutsky 56	Nagutskaya 56	6.0–9.0	51.0	HCO_3 75–90, (Na + K) > 90	CO_2(aq) 500–1000	Healing–table
2	55	Na-HCO_3-SO_4-Cl (HCO_3-SO_4)	Mid-Essentuki	Essentuki new-55	0.4–0.9	43.0	HCO_3 40–55, SO_4 20–35, Cl 20–30, (Na + K) > 80	–	Table
	2-b		Beshtaugorsky-2	Beshtaugorskaya-2	2.2–5.0	54.0	HCO_3 35–50, SO_4 35–50, (Na + K) 70–90	CO_2(aq) 500–800	Healing–table
3	66	Na-HCO_3-SO_4-Cl (SO_4-HCO_3-Cl)	Beshtaugorsky-1	Beshtaugorskaya healing	4.0–8.0	76.5	SO_4 30–45, HCO_3 30–45, Cl 20–30, (Na + K) 65–80	CO_2(aq) 500–1500	Healing–table
4	9	Na-Ca-HCO_3-SO_4	Buguntinsky	Buguntinskaya	0.2–0.9	14.0–33.0	HCO_3 40–55, SO_4 30–45, (Na + K) 60–75, Ca 25–35	–	Table
	69-bis-1, 1-south		Zheleznovodsky	Smirnovskaya	3.0–4.0	20.0–40.0	HCO_3 40–50, SO_4 30–40, (Na + K) 50–65, Ca 25–40	CO_2(aq) 800–1300	Healing–table
	69, 69-bis, 64, 59			Slavyanovskaya	3.0–4.0	54.0–58.0		CO_2(aq) 500–1000	Healing–table
5	70	Na-Ca-SO_4-HCO_3 (HCO_3-SO_4). H_2SiO_3	Gaazovsky	Dr. Gaaz	3.5–5.5	16.0	SO_4 40–60, HCO_3 30–50, Cl 19–25, (Na + K) 55–70, Ca 20–40	CO_2(aq) 1000–1700 H_2SiO_3 50–140	Healing–table
6	7-re, 107-d, 5/0, 5/0-bis, 2-b-bis	Ca-Mg-Na (Ca-Mg. Ca-Na-Mg) HCO_3-SO_4	Kislovodsky	Narzan	2.0–3.0	13.0–15.1	HCO_3 45–80, SO_4 20–50, Ca 30–60, Mg 20–30, (Na + K) 20–40	CO_2(aq) 1000–2500	Healing–table
	7, 5/0			Dolomite Narzan	4.0–4.5	14.7		CO_2(aq) 2000–2300	Healing–table
	8-bis, 23, 1-op, 2-pe-bis, 114-e, 115-e			Sulfate Narzan	5.0–5.5	15.3		CO_2(aq) 2000–2200	Healing–table

Table 4 continued

Nº	Well number	Mineral water group	Hydrogeochemical type of mineral water	Name of mineral water	TDS, g/L	T°C	Main ions, % meq/L	Balneological component, mg/L	Water use
7	1, 4, 7, 24	Na (Na-Ca) Cl-HCO_3-SO_4. H_2SiO_3	Pyatigorsky-1	Mashuk Nº. 1	4.0–5.5	27.0	Cl 30–45, HCO_3 20–45, SO_4 20–30, (Na + K) 55–75	H_2SiO_3 50–70; CO_2(aq) 1500–2000	Healing–table
	19		Pyatigorsky-2	Mashuk Nº. 19	5.5–6.5	52.0	Cl 40–50, HCO_3 20–40, SO_4 20–30, (Na + K) 60–75, Ca 20–30	H_2SiO_3 50–80; CO_2(aq) 500–1000	Healing–table
8	49	Na-HCO_3-Cl (Cl-HCO_3)	Nagutsky-4	Nagutskaya-4	6.0–9.0	38.4	HCO_3 70–80, Cl 20–25, (Na + K) > 95	CO_2(aq) 500–900	Healing–table
9	33-bis, 34-bis, 39-bis, 41-bis, 49-e, 418, 56, 57-re-bis, 71	Na-HCO_3-Cl (Cl-HCO_3). H_3BO_3	Essentuki # 4	Essentuki Nº. 4	7.0–10.0	14.0–53.0	HCO_3 55–80, Cl 20–45, (Na + K) > 80	H_3BO_3 30–60; CO_2(aq) 500–1800	Healing–table
	17-bis, 36-bis, 46		Essentuki # 17	Essentuki Nº. 17	10.0–14.0	14.0–38.0	HCO_3 55–75, Cl 35–45, (Na + K) > 90	H_3BO_3 40–90; CO_2(aq) 500–2350	Healing
	9-bis, 47		Essentuki # 17	Nagutskaya-17	10.0–14.0	41.0	HCO_3 55–75, Cl 35–45, (Na + K) > 90	H_3BO_3 30–80; CO_2(aq) 500–1200	Healing

These waters' main therapeutic properties are due to the high sodium concentration, which is about 60% meq/L. Such mineral waters are used for external and internal use, having a wide range of therapeutic parameters. Indications for referral to spa resorts with carbon dioxide baths are diseases of the circulatory system. If water is applied inside, it has a positive effect on the digestive tract, particularly on the stomach, liver, and kidneys.

Therapeutic effects of mineral waters

Caucasian mineral waters have great diversity in waters by ion and gas composition, conditions of formation, and healing properties. The significant parts of the mineral waters of the region are gases. They are mainly represented by CO_2, to a lesser extent N_2, H_2S, and CH_4. The optimal content of CO_2(aq) in mineral waters is 0.5–2.0 g/L. Due to these CO_2-bearing waters' high therapeutic properties, the Caucasian region quickly became widely known in Russia. High pCO_2 groundwater is now recognized as one of the most effective spa therapy methods for diseases of the cardiovascular system. The main balneological factor is dissolved carbon dioxide and physical–chemical parameters (Eh, temperature, and pH). CO_2 is continuously formed in the body tissues during metabolism and plays an essential role in regulating breathing and blood circulation. These waters also contain H_2SiO_3 and H_3BO_3. They are used in the form of baths, swimming pools, showers, various irrigation, inhalation, and drinking therapy (Kosyakov et al., 2012).

The mechanism of carbon dioxide waters' effect in *external* use consists of temperature and mechanical and chemical factors. The indications for referral to spa resorts with carbon dioxide baths are circulatory system diseases. In the external use of carbon dioxide mineral waters in the form of baths, there is a redistribution of blood, expansion of skin blood vessels, lowering blood pressure, increasing heart muscle contractility, and increasing tone of the parasympathetic nervous system (Fioravanti et al., 2017). The concentration of carbon dioxide in mineral waters used for baths is between 0.5 and 1.5–2.0 g/L; water temperature is 35–36 °C (*Carbon dioxide mineral..,* 1963). Water temperature has a significant effect on changing blood pressure. In some diseases (arterial hypotension, neurosis, neurocirculatory dystonia), the water temperature is reduced to 34–32 °C; the procedure is appointed after a day or 4–5 times a week, for the course of therapy 10–12 baths.

CO_2-bearing mineral waters are used *internally* for stomach washing and inhalations. The main form of internal application of mineral waters is drinking therapy. Mineral waters of TDS low (2.0–5.0 g/L) and medium (5.0–15.0 g/L) are used for drinking treatment; freshwater (TDS < 1.0 g/L) is used as table water. CO_2 makes the mineral waters taste good and better helps quench thirst. Simultaneously, carbon dioxide has a beneficial effect on the nervous system, exciting and toning it; it excites taste receptors in the mouth, increasing the appetite (Efimenko, 2015). However, indications and contraindications are determined by the doctor treating the case on an individual basis.

Zheleznovodsk Spa also has two profiles: diseases of digestive organs (chronic esophagitis; gastritis; stomach and duodenal ulcer; diseases of the operated stomach; chronic hepatitis; cholecystitis; pancreatitis; enteritis; colitis) and kidney and urinary tract diseases (chronic pyelonephritis; chronic focal nephritis; chronic cystitis; chronic nonspecific prostatitis; urinary stone disease).

Kislovodsk is an exceptional balneological and climatic spa, the main cardiological resort of Russia. Indications for treatment at this resort are circulatory system diseases (mitral valve insufficiency, coronary artery disease, hypertensive disease), respiratory organs (chronic bronchitis, bronchial asthma), diseases of the musculoskeletal system, gynecological diseases, and nervous system diseases (neuroses, atherosclerosis, nonspecific respiratory diseases) (Shogentsukova, 1986, Sinkevich, 2006).

Pyatigorsk resort is a multi-profile one. Patients with the following diseases are referred here for treatment: diseases of the peripheral nervous system, diseases of the musculoskeletal apparatus (spinal osteochondrosis, arthritis, osteoarthritis); diseases of digestive organs (see indications for Essentuki and Zheleznovodsk spas); skin diseases (psoriasis, eczema, neurodermatitis, hives, dermatitis, seborrhea), vascular diseases (atherosclerosis, varicose veins, vasculitis), and gynecological diseases (infertility, menopausal syndrome, endometriosis) (Efimenko, 2015).

Essentuki Spa's profile is to treat patients with gastrointestinal problems, metabolic disorders, and liver diseases. Essentuki has specialized sanatoriums for the treatment of children, teenagers, and adults who have diabetes. Therapeutic mineral waters (Essentuki #4. Essentuki #17) are used in the treatment of diseases of the stomach and duodenum (chronic gastritis, chronic gastroduodenitis; gastric and duodenal ulcer), esophageal diseases (chronic esophagitis, reflux esophagitis), intestinal diseases (functional disorders; chronic enteritis; colitis); diseases of the liver and biliary tract (viral and chronic hepatitis in the inactive phase, chronic cholecystitis; dyskinesia of the gallbladder and biliary tract), pancreatic diseases (chronic pancreatitis of mild to medium intensity), and metabolic diseases (constitutional obesity, diabetes mellitus). The resort also treats related diseases of the ear, gutter, nose, gynecological, and urological disorders (Efimenko & Fedorova, 2013; Uiba et al., 2016).

Conclusion

Thus, the Caucasian mineral water region is very attractive area from balneological point of view, so there are a wide range of mineral waters with various ions and dissolving gas phases within restricted area. However, the dominant type of mineral water here is CO_2-rich water enriched with H_2SiO_3 and H_3BO_3. The CMW region includes four famous spa centers with a different therapeutic profile: Zheleznovodsk, Kislovodsk, Pyatigorsk, and Essentuki cities. Spa treatment is based on the use of different types of mineral waters, therapeutic muds within the region's diverse landscapes, and climatic conditions. Based on hydrochemical features, we specified 9 groups and 16 types of mineral waters and each water type presents particular therapeutic interest and could utilize for treatment during gastrointestinal problems, metabolic and nervous system disorders, various diseases of liver, kidney, and so on.

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Data availability All data are original and were obtained by the authors. The data do not contain any prohibited for publication results.

Declarations

Conflict of interest No conflict of interest.

Human or Animal rights No animal research was performed when the article was prepared.

Consent to participate All authors consent to participate.

Consent to publish All authors consent to publish before reference in the manuscript.

References

Aires-Barros, L., Marques, J., Graça, R. C., Matias, M. J., Van Der Weijden, C. H., Kreulen, R., & Eggenkamp, H. G. M. (1998). Hot and cold CO_2-rich mineral waters in Chaves geothermal area (Northern Portugal). *Geothermics, 27*(1), 89–107. https://doi.org/10.1016/s0375-6505(97)84483-5

Albertini, M. C., Dacha, M., Teodori, L., & Conti, M. E. (2007). Drinking mineral waters: Biochemical effects and health implications - The state-of-the-art. *International Journal of Environment and Health, 1*(154), 153–169. https://doi.org/10.1504/IJENVH.2007.012230

Albu, M., Banks, D., & Nash, H. (1997). Mineral and thermal groundwater. *Resources*. https://doi.org/10.1007/978-94-011-5846-6

Aquilina, L., Ladouche, B., Doerfliger, N., Seidel, J. L., Bakalowicz, M., Dupuy, C., & Le Strat, P. (2002). Origin, evolution and residence time of saline thermal fluids (Balaruc springs, southern France) implications for fluid transfer across the continental shelf. *Chemical Geology, 192*(1–2), 1–21. https://doi.org/10.1016/s0009-2541(02)00160-2

Back, W., Landa, E. R., & Meeks, L. (1995). Bottled water, spas, and early years of water chemistry. *Ground Water, 33*, 605–614.

Batalin, F. A. (1861). *Pyatigorsk region and the Caucasian mineral waters* (Vol. 1, 2) (in Russian). Saint Petersburg.

Borović, S., Marković, T., Larva, O., Brkić, Ž., & Mraz, V. (2016). Mineral and thermal waters in the croatian part of the Pannonian Basin. In P. Papic (Ed.), *Mineral and thermal waters of southeastern, Europe environmental earth sciences.* Springer. https://doi.org/10.1007/978-3-319-25379-4_2

Carbon dioxide mineral waters of the North Caucasus (1963). (Under the ed. I.Panteleev), Moscow, Pub. USSR Academy of Sciences.

Davis, S. N., & Davis, A. G. (1997). Saratoga Springs and early hydrogeochemistry in the United States. *Ground Water, 35*, 347–356.

Efimenko, N. V. (2015). Action mechanisms of drinking mineral waters and their role in resort gastroenterology. *Resort Medicine, 3*, 2–7.

Efimenko, N. V., & Fedorova, T. E. (2013). Drinking mineral water of the Essentuki type in medical rehabilitation of patients by not alcoholic fatty illness of a liver at a sanatorium stage. *Resort Medicine, 2*, 24–26.

Filimonova, E., Lavrushin, V., Kharitonova, N., et al. (2020). Hydrogeology and hydrogeochemistry of mineral sparkling groundwater within Essentuki area (Caucasian mineral water region). *Environmental Earth Sciences*. https://doi.org/10.1007/s12665-019-8721-2

Fioravanti, A., Karagülle, M., Bender, T., & Karagülle, M. Z. (2017). Balneotherapy in osteoarthritis: Facts, fiction and gaps in knowledge. *European Journal of Integrative Medicine, 9*, 148–150.

Gaas, F. P. (1811). Ma visite aux eaux d'Alexandre en 1809 et 1810 (in French). My voyage to Alexander waters from 1809 to 1810. Moscow.

Glukhov, A. N. (2013). 220-anniversary of the visit to Caucasian mineral waters by academician Pallas P.S. *Resort Medicine, 1*, 88–92.

Grassi, M., Lucchetta, M. C., Grossi, F., & Raffa, S. (2002). Possibilities of thermal medicine in gastrointestinal functional disorders. *Clinica Terapeutica, 153*, 195–206.

Grigoriev, N. A., & Chernetsov, A. I. (2010). *Mineral'nye istochniki Severnogo Kavkaza i ih gidrologicheskoe ispol'zovanie*. Mineral Sources of the North Caucasus and Their Hydrological Use. (in Russian).

Ivanov V.V., & Nevraev G.A. (1964). Klassifikatsia mineralnyh podzemnyh vod (in Russian). *Classification of Mineral groundwater*. Moscow, Nedra.

Ivanov, V.V. (1972). Kavkazskie mineral'nye vody. Izd. Tsentral'nogo instituta kurortologii i fizioterapii. T. 21 (in Russian) *Caucasian mineral water.* Moscow, pub. Central Institute of balneology and physiotherapy.

Kosyakov, L. S., Velikanov, I. I., Drobchuk, I. A., & Hubiyev, FKh. (2012). Carbonic mineral baths influence with various concentration of carbonic acid on brain blood circulation, vegetative regulation of patients heart with initial manifestations of vascular and brain insufficiency. *Resort Medicine, 4*, 62–65.

Kralj, P., & Kralj, P. (2000). Thermal and mineral waters in north-eastern Slovenia. *Environmental Geology, 39*, 488–500. https://doi.org/10.1007/s002540050455

Lavrushin, V.Y. (2012). Podzemnyye flyuidy Bol'shogo Kavkaza i ego obramleniya (in Russian). In: Polyak BG (ed) *Subsurface fluids of the Greater Caucasus and its surrounding*. GEOS, Moscow.

Lavrushin, V. Y., Lisenkov, A. B., & Aidarkozhina, A. S. (2020). Genesis of the Essentuki carbon dioxide field (Northern Caucasus) (in Russian). *Geochemistry, 65*(1), 75–91. https://doi.org/10.31857/S0016752520010082

National State Standard R 54316—2011. (2011). *Natural mineral drinking waters*.

Nelyubin, A. P. (1825). *Complete historical, medical and topographical, physical and chemical and medical description of the Caucasian mineral waters* (Vol. 1, 2) (in Russian). Saint-Petersburg.

Ovchinnikov, A. M. (1947). *Mineral waters* (in Russian). Moscow, Pub. Gosgeolizdat.

Panteleev, I. Y. (1963). *Essentuki salt-alkaline waters in the system of Caucasian mineral waters* (in Russian). Moscow: Pub. USSR Academy of Sciences.

Petraccia, L., Liberati, G., Masciullo, S. G., Grassi, M., & Fraioli, A. (2006). Water, mineral waters and health. *Clinical Nutrition, 25*(3), 377–385. https://doi.org/10.1016/j.clnu.2005.10.002

Porowski, A., Romanova, A., Gebus-Czupyt, B., Wach, B., & Radzikowska, M. (2021). Stable hydrogen and oxygen isotopic composition of bottled waters in Poland: Characterization in the context of different market categories and implications for the origin authentication and natural isotopic quality preservation. *Journal of Geochemical Exploration, 220*, 1–14. https://doi.org/10.1016/j.gexplo.2020.106684

Potapov, E. G., & Danilov, S. R. (2012). History of Essentuki carbonic mineral water deposits studies (in Russian). *Resort Medicine, 3*, 9–12.

Quattrini, S., Pampaloni, B., & Brandi, M. L. (2016). Natural mineral waters: chemical characteristics and health effects. *Clinical Cases in Mineral and Bone Metabolism, 13*(3), 173–180. https://doi.org/10.11138/ccmbm/2016.13.3.173

Shinkarenko, A.L. (1946). Hydrogeochemical Characteristics and Genesis Issues of Essentuki Carbon Acid Waters (in Russian) *Proceedings of the State Balneological Institute at CMW*. Pyatigorsk, Vol. XXIII-XXV, 457–460.

Shogentsukova, E.A. (1986). Adaptatsia reaktsii patsientov s bronhial'noi astmoi na uslovia Priel'brus'ya (in Russian). Adaptation reaction of patients with bronchial asthma in the conditions of the middle Elbrus region. In *Adaptation and resistance of the organism in the conditions of the mountain climate* (pp. 185–196). Kiev, Naukova Dumka.

Siegel, D. I. (1996). Natural bubbling brew: The carbonated springs of Saratoga. *Geotimes, 41*(5), 20–23.

Siegel, D. I., Bickford, M. E., & Orell, S. (2000). Leachate, marine and bedrock water sources in the Fresh Kills Landfill, Staten Island, New York: Constraints on an environmental problem from Pb and Sr isotopic and other geochemical data. *Applied Geochemistry, 15*, 493–500.

Sinkevich E. (2006). Lechenie minerel'noi vodoi na kurortah Kavkazskih mineral'nyh vod (in Russian). *Mineral water treatment at the Caucasian mineral water (CMW) resorts.* Guide for visitors to the CMW resorts.

Soprun, D. S., & Reps, V. F. (2013). Drinking mineral water as a means of metabolic care. *Resort Medicine, 1*, 61–64.

Stier-Jarmer, M., Kus, S., Frisch, D., Sabariego, C., & Schuh, A. (2015). Health resort medicine in non-musculoskeletal disorders: Is there evidence of its effectiveness? *International Journal of Biometeorology, 59*(10), 1523–1544. https://doi.org/10.1007/s00484-015-0953-6

Uiba, V. V., Efimenko, N. V., & Potapov, E. G. (2016). Resorts of the caucasian mineral waters in the early 21st century. *Resort Medicine, 1*, 1–6.

Van der Aa, M. (2003). Classification of mineral water types and comparison with drinking water standards. *Environmental Geology, 44*, 554–563. https://doi.org/10.1007/s00254-003-0791-4

Voronov, A. N. (2000). Some features of mineral waters in Russia. *Environmental Geology, 39*(5), 477–481.

Vrba, J. (1996). Thermal mineral water springs in Karlovy Vary. *Environmental Geology, 27*, 120–125.

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