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Sources of Solutes in Low-Enthalpy Mineral Waters of Essentuki Spa (the Caucasian Region, Russia)

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ABSTRACT

The Essentuki mineral groundwater (EMGW) basin involves the unique wide variety of mineral waters having different TDS, pH, chemical, and gas composition. TDS changes from fresh (0.5-0.9 g/l) to high-salinity (10-13 g/l) and strongly depends on the chemical composition of water. The region is characterized by a widespread of high pCO_2 sparkling Ca-Na-HCO_3-Cl waters, which are a trademark as «Essentuki 4» and «Essentuki 17», and has strong therapeutic properties. Geothermal conditions, major and microelements, isotopic characteristics of water ($\delta^{18}O$ and δ^2H), and gas ($\delta^{13}C$ in CO_2 and CH_4, $^3He/^4He$) phases of carbon dioxide mineral waters of EMGW basin are considered.

1. INTRODUCTION

The Caucasian mineral water (CMW) region is the unique spa area in the Russian Federation, known by therapeutic mineral springs. The Essentuki mineral groundwater basin is located in the central part of the CMW region. The study of mineral groundwater has more than 200 years of history. The first documents about saline springs are dated by 1810 when doctor F.P. Gaas found and depicted three springs. Then, in 1823, professor A.P. Nelyubin described 28 springs (Potapov & Danilov, 2012). The springs No 4 and No 17 were found the most valuable and were called Essentuki-4 and Essentuki-17, famous now all over the world.

The Essentuki mineral groundwater area includes a lot of types of mineral waters with different TDS, pH, chemical, and gas composition. TDS is caused by the water chemical composition and varies from fresh (0.5-0.9 g/l) to high-salinity (10-13 g/l). According to the main anion, the chemical type of groundwater changes from HCO_3 to Cl-HCO_3 or SO_4-HCO_3. Based on gas content, the mineral groundwater within the Essentuki basin could be still water or high-pCO_2 water, sometimes H_2S rich aqua. At the same time, the most interesting ones are carbon dioxide bicarbonate-chloride sodium waters, which are known as «Essentuki 4» and «Essentuki 17», widespread in upper Cretaceous and Paleogene sediments. They have long been used in balneology, as well as for bottling as therapeutic-table water. Due to the high therapeutic properties of these carbon dioxide waters, the Essentuki resort quickly became widely known in Russia. The water of similar composition, found in other places, became known as the waters of the «Essentuki» type.

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

This study was undertaken to identify the source of water and gas phases in mineral groundwaters from EMGW.

2. STUDY AREA

The investigated area is located in the Russian Federation, in the southern part of the Stavropol region, near the northern branches of Greater Caucasus, between the Black and Caspian seas (Fig.1). The main object of study – is a part of the Mineralovodsky artesian basin (10.2 thousand km^2), located in the center of the CMW (Caucasian mineral water region - about 5.2 km^2), called the Essentuki mineral water area. Essentuki - is one of the spas of the CMW region. Besides, there are several other: Mineralnye Vody, Zheleznovodsk, Kislovodsk, and others.

The Essentuki mineral water area of 130.75 km^2 is located in the northwest of the CMW northwest of the confluence of the rivers Bugunta and Podkumok. The main water stream is a mountain river Podkumok, which flows from southwest to northeast. Its average flow rate is about 2.8 m^3/s, at maximum - about 235 m^3/s. The rivers are fed by precipitation, melting of snowfields, and glaciers in the mountains outside the CMW region. Winter low water lasts from January to March, summer - from July to September. In low-water periods, most small streams in the area dry out.

Different high-altitude position, different degree of relief ruggedness, the combination of open and closed areas, and the laccolite-peaks existence create microclimatic zones inside the CMW. The climate of the EMGW basin is continental, mountain-steppe. Winter is not cold, thaws are often with a positive temperature, but there may be frosts down to −33 °C. The average January temperature is −4.2 ° C. Often, there are days with fogs (in November and December, 13-14 days). Spring is very short, as early as April comes the temperature quickly rises, the last night frosts usually occur in mid-April. The summer is warm, with lots of hot and dry days. The average temperature in July is + 20.4 ° C, and the maximum temperature reaches +37 ° C. The average precipitation is - 536 mm, about 45% of which is from May to July (Savelieva, 1987). The total potential evapotranspiration is 400-450 mm. The area's wetting coefficient (ratio of precipitation to evaporation) varies from 0.7 in the flat part to 1 or more in the mountainous area, which makes it possible to assign the basin territory as a good-rainfall zone.

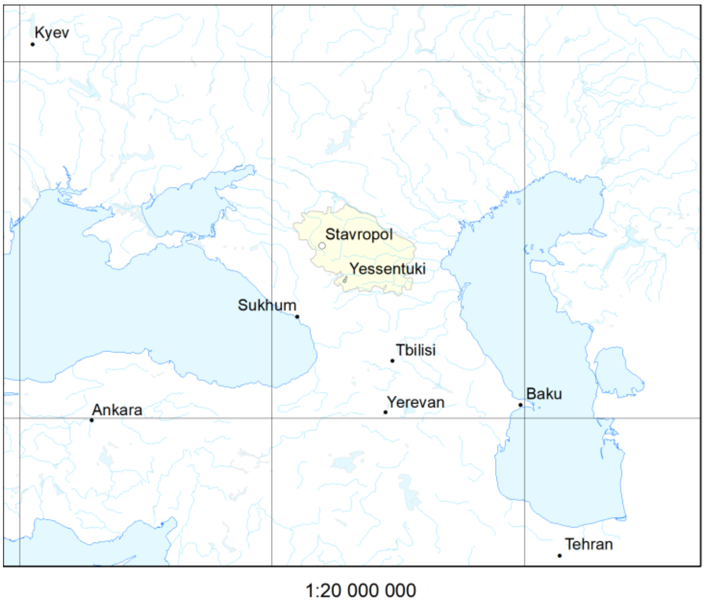

Figure 1. The location of the study area.

2. GEOLOGICAL SETTING

The CMW region locates on the joint between the northern part of the Greater Caucasus mega-anticlinorium and the Scythian (Pre-Caucasian) epi-Hercynian plate. The boundary between structures passes in the north along the Cherkesskaya flexure-fractured zone and a fragment of the regional Armavir-Nevinnomyssk depth fault, in the northeast and east - along the Nagutsko-Lysogorskaya flexure-fractured zone. The Essentuki mineral water area is located within the North Caucasian monocline, complicated with the large basement structure Transcaucasian uplift. This uplift of the basal complex produces a wide (up to 60 km) and flat anticline in the sedimentary cover. The EMWA is disposed to the crown of this anticline, which is accompanied by the Kislovodsk-Kumagorsky fracturing zone. Most of the mineral water basins are associated with the area of intensive breaking, like Kislovodskaya, Essentuksko-Novo-Blagodarnenskaya, Zheleznovodskaya, and others. The Essentuksko-Novo-Blagodarnenskaya zone is a structural extension, consisting of linear narrow horsts and grabens, restricted north-eastern faults. The low-amplitude semi-circular fault zones and associated zones of increased tectonic fracturing in sedimentary rocks, surrounding the volcanic mountains from the south and west, are the most hydro geologically active as water-conducting channels and ways for CO_2 transport. The depth of basal complex within Transcaucasian uplift is shallow and equal to 1-2 km by contrast to enclosing depressions, where the basement lies at shallow depths of 3-8 km. The Proterozoic-Palaeozoic basement has a block structure and is composed of sedimentary-metamorphic and erupted rocks (granites, granodiorites, shales, gneisses, amphibolites, tuffs, sandstones, conglomerates, etc.). Rocks are strongly crumpled and fractured.

The CMW region is characterized by an active geodynamic regime and high seismic intensity. At depths of about 15-20 and 35-45 km are zones of heating, deconsolidation, and partial melting of rocks, catalyzing produce of carbon dioxide.

3. HYDROGEOLOGICAL SETTING

The hydrogeology section of the CMW region is represented by the monoclinal layers of Meso-Cenozoic aquifers going down towards the aquitards Proterozoic-Palaeozoic basement (Fig.3). The recharge occurs in the southern and southwestern mountainous parts of the region, represented by the system of the Upper Jurassic and Cretaceous cuestas. The rest of the area, covered primarily by waterproof Maikop sediments, are represented by Upper Jurassic and Cretaceous sediments, which are the main domains of the water transit and discharge. Mainly, water permeability and the diverse lithological composition of sedimentary rocks define the heterogeneity of the aquifer hydraulic properties. The principal aquifers of EMWA are following (Fig.2):

- The Danish-Zealand aquifer (₽$_{1d\text{-}sl}$)

- The Upper Cretaceous aquifer (K_2)

- The Lower Cretaceous aquifer ($K_{1a\text{-}al1}$)

- The Titon-Valanginian aquifer (J_{3tt}-K_{1v}).

4. HYDROCHEMISTRY

Within the Essentuki mineral groundwater basin, the wide variety of mineral waters with different temperatures, TDS, pH, chemical, and gas composition occur. The temperature of mineral waters ranges from 10 to ~ 70 °C and depends strongly on the depth and position of aquifers. The temperature of the waters increases in the northerly direction, reflecting the descend of water-bearing sediments. In the near-surface zone, there is shallow cold mineral water with low TDS and Na-HCO_3-Cl chemical type

(Fig. 4). That is why the local geothermal gradient is approximately 40-42 °C per km. There is a direct correlation between water temperatures and the aquifer depth (Fig. 3). The water Tmin is close to the mean annual air temperature. The data points above the trend line can be explained by the possible mixture of groundwater from multiple aquifers.

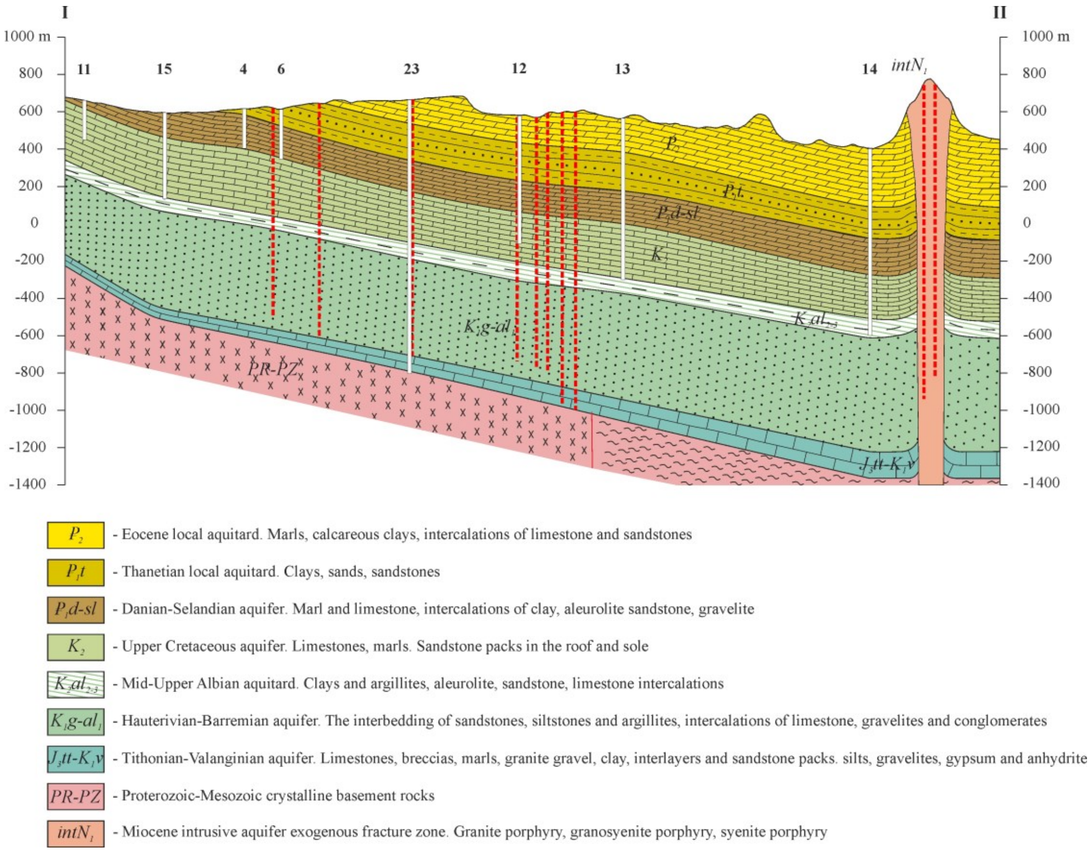

Figure 2. The cross-section of the Essentuki mineral groundwater basin with the sampling points.

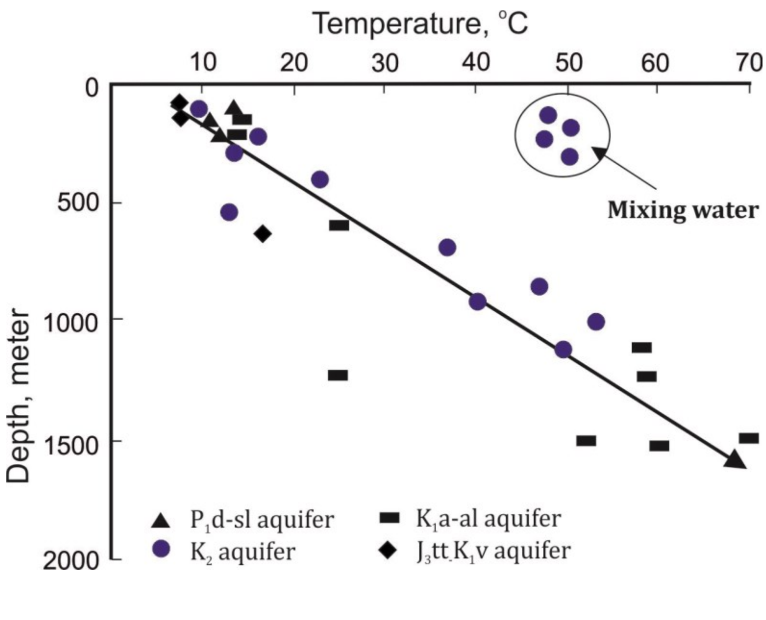

Figure 3.The correlation between the measured temperatures of the water and the depth of the aquifer. The straight line is a standard increasing of temperature of aquifer due to the local temperature gradient.

The pH of mineral waters from all complexes is weakly alkaline and varied from 6.3 to 7.2. TDS changes from fresh (0.5-0.9 g/l) to high-salinity (10-13 g/l) and strongly depends on the chemical composition of water. The chemical composition of mineral waters mainly depends on the lithological composition of water-bearing rocks and the constituents of the gas phase. Besides, the interfacial overflows and the degree of hydrogeological openness of the horizon influence the geochemical feature of the waters. All of these factors lead to the formation of mineral waters with various chemical compositions within the same aquifer complex (table 1).

Table 1. Chemical composition of groundwater samples in the study area

Sampling point	Aquifer	T, °C	pH	TDS	Na^+	K^+	Ca	Mg	HCO_3	SO_4	Cl	Br	H_3BO_3	H_2S
				g/l								mg/l		
1	Ꝑ1d-sl	14	6,6	12,8	3,69		0,128	0,082	6,33	<0,02	2,48	1	68	-
2		15	6,5	12,5	3,57		0,126	0,089	6,21	<0,02	2,38	2	66	-
3		15	6,8	9,5	2,78		0,078	0,046	4,61	<0,02	1,88	1	63	4,5
4		16	6,4	8,8	2,46		0,146	0,07	4,37	<0,02	1,72	1	40	-
5		14	6,4	8,6	2,39		0,153	0,058	4,33	<0,02	1,61	1	50	-
6		14	6,5	9	2,53		0,132	0,065	4,57	<0,02	1,66	2	44	-
7		15	6,5	9,1	2,52		0,14	0,076	4,61	<0,02	1,68	2	49	-
8		13	6,4	8,5	2,34	0,02	0,07	0,051	4,26	<0,0001	1,69	5,9	40	-
9		15	6,4	8,8	2,44		0,153	0,075	4,38	<0,02	1,7	2	45	-
10		15	6,4	8,1	2,33	0,01	0,113	0,06	4,13	0,008	1,47	4,6	50	-
11	K_2	13	7,2	0,6	0,17	0,00	0,005	0,001	0,37	0,047	0,03	0,1	4	-
12		37	7	9,8	2,83	0,02	0,057	0,063	5	0,002	0,75	4,2	-	-
13		43	6,2	8,2	2,45	0,02	0,044	0,025	4,02	0,007	1,64	5,5	-	-
14		44	7,7	9,4	2,46	0,02	0,039	0,026	4,49	<0,0001	1,69	5,4	-	-
15		21	7	1,2	0,35	0,01	0,031	0,01	0,57	0,025	0,21	0,7	2	7,8
16		21	6,9	2,7	0,69		0,058	0,026	1,55	<0,020	0,33	4	3	13
17	K_1a-al	16	7	0,6	0,12		0,04	0,012	0,23	0,134	0,04	0,2	1,4	-
18		43	7,2	0,7	0,17		0,003	<0,01	0,29	0,121	0,07	0,2	1	5
19	J_3tt-K_1v	22	7	2,5	0,87		0,202	0,045	0,22	0,831	0,03	0,8	-	-
20		45	6,3	6,5	0,74		1,093	0,211	2,7	0,859	0,83	3,6	4,7	-
21	surface water	12	5,7	-	0,10	0,00	0,062	0,039	-	0,22	0,06	0,1	-	-

According to the main anions, the chemical type of groundwater varies from HCO_3 to Cl- HCO_3 or SO_4- HCO_3 (Fig. 4).

In the Lower Paleocene (Danish-Zeland, Elburgan) aquifer (Ꝑ$_{1d-sl}$), the predominantly cold sparkling waters with TDS from 7 to 10 g/l widely spread. According to contents major ions, these water are preferably a Na-HCO_3-Cl type. The escaped gas presented mainly CO_2 60-98%; CH_4 3-22%; N_2 1-36%, O_2 0.1-2.0%.

The mineral waters circulated in the Upper Cretaceous aquifer (K_2) is rather warm with a that TDS varied from 0.5 to 6.3 g/l, and these preferably belong to the Na-HCO_3-Cl type. The TDS of these waters is strongly reflected in the pumping rate and increases with the rate up. In escaped gas, the CO_2 gas prevails (varies from 28 to 80 vol.%), the second one is CH_4 (up to 34 vol.%). The content of CO_{2dis}. ranges from 0.2 to 1.9 g /L and H_2S_{dis}. is varied from 0.012 to 0.019 g /l. The gas factor is low (up to 0,85). The decrease of the mineral water rate results to decrease in CO_2 content.

The Lower Cretaceous aquifer (K_{1a-al}) is bound warm mineral waters with a TDS that varied from 0.5 to 6 g/l. These geochemical water types change from Ca-Mg-Na-SO_4-Cl-HCO_3 to Na-SO_4-Cl-HCO_3. Groundwater contains in increased amounts: a) silica (H_2SiO_3 up to 45.5 mg/L); and b) iron (up to 5.2 mg /L). Groundwater contains dissolved hydrogen sulfide (up to 2.2 mg/L). The composition of the spontaneous gas contains helium, oxygen, methane, and carbon dioxide, but most of it belongs to nitrogen. The temperature of the water at the surface is significantly lower than the reservoir; it rises with an increase in the water withdrawal rate and varies within + 16.7 ... + 43.0 ° C.

The Titon-Valanginian aquifer (J_{3tt}-K_{1v}) contents thermally moderately mineral water with Cl-HCO_3 (SO_4-Cl-HCO_3) Ca-Mg-Na (Na-Ca) type. Groundwater salinity varies from 7.0 to 8.5 g/L. Groundwater contains in elevated quantities: a) carbon dioxide (CO_2 0.5-1.6 g/L); b) silicic acid (H_2SiO_3 up to 91 mg/L) and is characterized by high gas saturation. The gas factor varies from 15 to 30. Spontaneous gases are mainly carbon dioxide, nitrogen, methane, and oxygen.

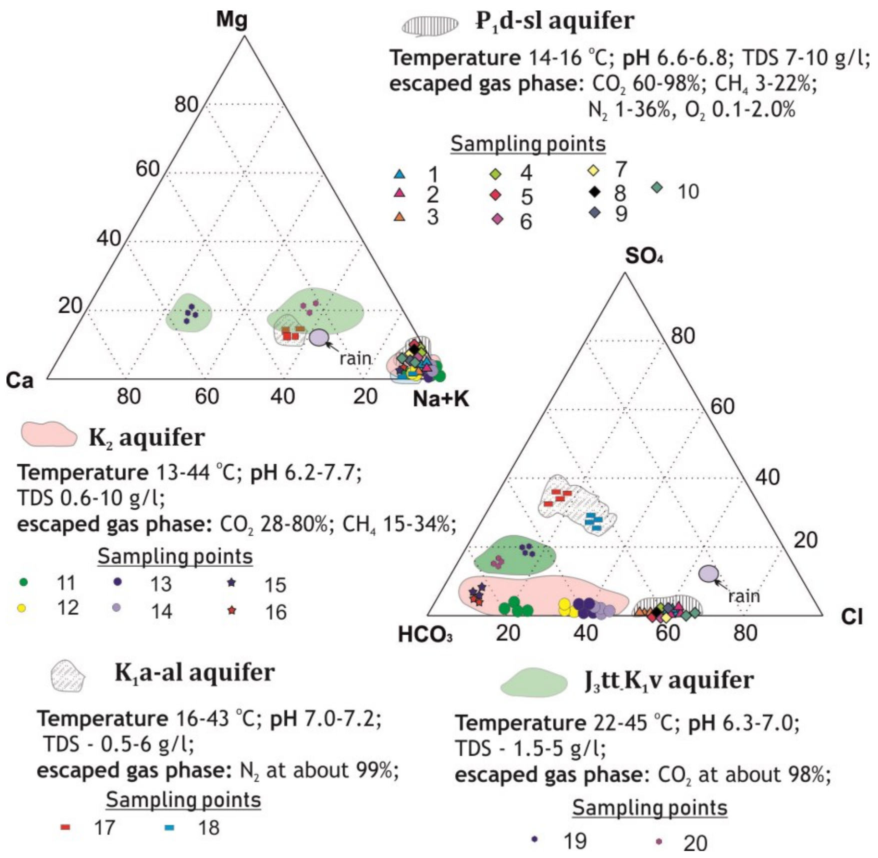

Figure 4. Major elements composition of the investigated waters. The sampling point is identical to the well's number in figure 2.

Based on gas content, the mineral groundwaters within the Essentuki basin could be still water or high-pCO_2 sparkling water, sometimes H_2S rich aqua. This study was undertaken to identify the source of water and gas phases in mineral groundwaters from EMGW. A wide range of TDS characterizes mineral waters that changed from 0.6 to 15.2 g/l. The mineral waters that interact with infiltration waters have the lowest TDS (< 2 g/l). In general, there is a trend towards an increase in TDS in the northerly direction.

The inversion of TDS is clearly visible in the Upper Cretaceous aquifer (K_2) in the Essentuki area. Mineral waters have a brand name, «Essentuki 4», and «Essentuki-17» are withdrawn from this aquifer. According to our data, the average TDS here is ~10 g/l, while TDS is characterized by ~4.5 g/l in the underlying aquifers. The main anion of mineral waters within the Essentuki area is almost always the HCO_3 ion (Fig. 4). The amount of this ion ranges from 35 to 81 mg-eq%. The composition of the other anions and cations strongly depends on the aquifer rock where mineral waters circulated.

The most contrasting differences in the composition of aquifers are observed by sulfate ion. For example, the proportion of sulfate ion among anions varies from ~20 to 40 mg-eq% in the J_{3tt}-K_{1v} aquifer. In absolute terms, its concentration here reaches 1.5-2 g/l. Obviously, this is due to the presence of gypsum clays and sandstones in the Late Jurassic sediments. Aquifer systems of the study area are quite different in concentrations of HCO_3 and Cl-ions. Maximum concentrations of HCO_3 ion (up to 5.6 g/l) are typical for waters of the late Cretaceous aquifer.

The most significant differences in the composition of waters associated with Upper Cretaceous aquifer (K_2) and older complexes are observed in the concentration of chlorine ion. For example, if in the Titon-Valanginian aquifer (J_{3tt}-K_{1v}), the concentration of chlorine ion is significantly below 1 g/l, in Upper Cretaceous aquifer (K_2) of Essentuki area, it reaches nearly 2 g/l. Probably, the increased concentration of chlorides in the waters of Upper Cretaceous aquifer (K_2) is associated with the salt complex of sedimentation waters of marine genesis. This sedimentation is partially preserved in poorly permeable blocks of massive limestone K_2. Between the concentrations of chlorides and hydro carbonates, there is a direct functional relationship, which probably reflects the processes of dilution of mineral waters with a high content of chlorides and hydrocarbonates with low-salt water of atmogenic genesis. Obviously, these processes also reflect the dependence of the chlorine-ion concentration in the water on the depth of the well. Low calcium concentrations are typical for the waters of Upper Cretaceous aquifer (K_2). Sodium dominates among cations (>90 mg-eq%).

In general, the macro-component composition of the groundwater is quite different. The J_{3tt}-K_{1v} aquifer in the composition of anions is characterized by the presence of high concentrations of sulfate ion. According to the cation composition, there are different types of waters Ca-Mg-Na, Ca-Na, Na-Ca, but, in general, a significant role of Ca^{2+} ions is typical for them. The waters of the Upper Cretaceous aquifer (K_2) of the Essentuki area («Essentuki 4» and «Essentuki 17») contrast with the waters of these aquifers. It is characterized exclusively by the HCO_3-Cl-Na water type, in which the sulfate ion content is analytically undetectable by ICP-MS (<17 μg/l by S). However, they contain a higher concentration of HCO_3 and Cl-ions than in the underlying aquifers.

The mineral waters located in the J_{3tt}-K_{1v} aquifer have significantly higher contents of K, Si, Rb, Cs, Mn, Fe, Zn, Sr than the waters from K_2 sediments, although B, Ba, and Br enrich latterly.

5. ISOTOPIC COMPOSITION

The isotopic composition of water oxygen ($\delta^{18}O$) varies in the range from -14.3 to -7.4 ‰, and hydrogen – from -100 to -63 ‰. On the diagram δ^2H-$\delta^{18}O$ (Fig. 5) it can be seen that the figurative points of mineral waters are mainly dropped along the line of meteor waters (Craig's line). This is consistent with the previously obtained results of studies of the isotopic characteristics of mineral waters of the Essentuki area, which showed that the main part of the water balance of mineral water source is infiltrated meteor waters. We found a good correlation for $\delta^{18}O$ and δ^2H with concentrations of Cl, HCO_3, Ca, Mg, Na. These reflect the process of mixing isotope-light oxygen fresh meteoric waters and high-salt waters (possible sedimentogenec) with higher values of $\delta^{18}O$ and δ^2H. The latter can probably have a sedimentary genesis and, obviously, their mixing and causes an «oxygen» shift in the diagram δ^2H-$\delta^{18}O$.

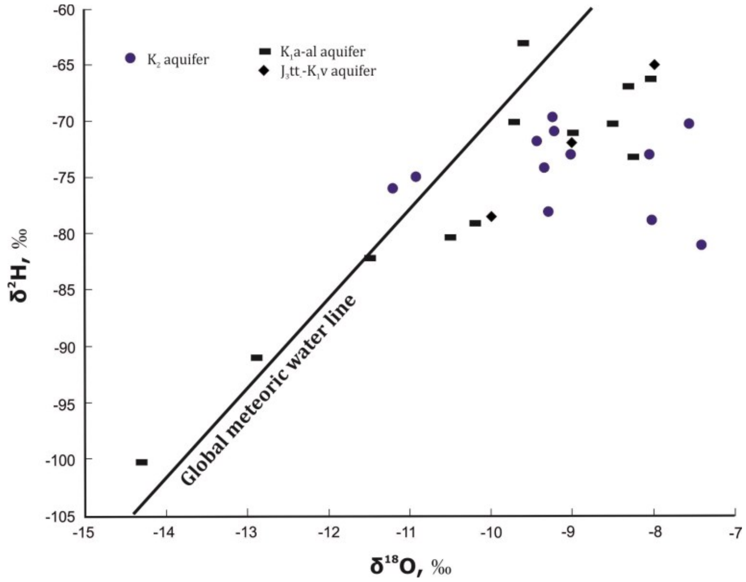

Figure 5. The plot of $\delta^{18}O$ and δD for mineral waters within the Essentuki area

6. GAS PHASE

6.1 Chemical composition

Gases represent an essential component of the EMGW mineral waters. They are mainly composed of carbon dioxide and, to a lesser extent, nitrogen, hydrogen sulfide, and methane. Samples of free associated gas were collected in glass tubes by the replacement method. The gas composition was determined by gas chromatography (Crystal-2000) using standard gas mixtures for the calibration (Lavrushin et al., 2012). Carbon ($\delta^{13}C(CO_2)$ and $\delta^{13}C(DIC)$) were carried out by mass spectrometry at the Geological Institute RAS (Moscow). CH_4 gas isotopes ratios were determined by isotope-ratio mass spectrometry MAT-253 using a Trace-GC gas chromatograph at the Geologica Institute of RAS.

In the Essentuki area dominated by carbon dioxide water, the share of CO_2 in the gas phase reaches 98%. However, there are also waters with high concentrations of methane (up to 44 %) and nitrogen (up to 70-90%). Methane in gases of the mineral water has insignificant concentrations (from 4 to 44%) in the central and southern parts of the Essentuki area. Its high concentrations are typical for wells that uncover water only of the Apt-Albian and Upper Cretaceous aquifer. It is present in all gas samples of the Essentuki area (from 4 to 20 %). The maximum concentration of CH_4 at the Essentuki area is noted in the gases of the well from which «Essentuki 17» is poured.

High nitrogen concentrations (up to 98 %) are typical for the waters with low TDS (min < 2 g/l). Here its appearance can be associated with shallow circulation waters enriched with a nitrogen of atmospheric genesis. Along with that, fairly high concentrations of the gas (2 to 32,6%) are detected in the carbon dioxide-methane gas of Essentuki and Nagutsky area. There is a direct relationship between methane concentrations (at CH_4 > 4 %) and nitrogen. On the other hand, it can reflect the dilution of these gases with carbon dioxide, and on the other – indicate the not atmogenic genesis of nitrogen in the gases of the Northern part of the Essentuki area. It, like methane, can be formed during the decomposition of organic matter.

Helium is present in gases at concentrations from <0,01 to 1,3 %. Helium concentration is constantly increasing in the Northern direction – with increasing depth and degree of hydrogeological closure of aquifers. Probably, for this reason, it is correlated with methane concentration.

Obviously, this dependence reflects the paragenetic relationship between the concentrations of these gases. They are characterized by the similarity of geological conditions favorable for their accumulation. These conditions are hydrogeological closure of aquifers, elevated temperatures and a long time of water in the reservoir. In addition, this dependence can be the consequence of dilution gases in sedimentary strata of the other gas, containing very low concentrations of nitrogen, methane, and helium. This gas is obviously magmatogenic carbon dioxide.

6.2 Isotopic composition

The value of $\delta^{13}C$ in the methane changes from -61,7 to -29,5‰. This value of $\delta^{13}C$ gases forms three isolated groups. The first group is characterized by maximum values $\delta^{13}C$ (CH_4) at minimum concentrations of methane (0,4-0,5 %). Other figurative points form two compact groups. One of them is characterized by the range of values $\delta^{13}C$ (CH_4) from -42.6 to -40.8 ‰, and the other from -61,7 to -59,6 ‰. The intermediate position between these groups is occupied by only one point with the value of $\delta^{13}C$ (CH_4) = -48,4‰. The second group combines gas samples exclusively from the Apt-Albian aquifer. The third group includes only gases from wells of the Essentuki area («Essentuki 4» and («Essentuki 17»).

The isotopic composition of carbon dioxide in the gas phase of mineral waters varies in the range from -16,7 to -4,3 ‰. In the waters of the Essentuki area, there is an inverse relationship between the value of $\delta^{13}C(CO_2)$ and the fraction of HCO_3 in the composition of the anions. That is, the gas composition of waters of the Essentuki type (HCO_3-Cl-Na type) is characterized by the presence of carbon dioxide with an admixture of isotope-light (biogenic) CO_2. It is formed by oxidation of organic matter. This emphasizes the important role of the biogenic processes in the formation of the «salt-alkaline» type of these waters.

The carbon dioxide with lower values of $\delta^{13}C$ (< -8 ‰) is found in gases that are rich in methane (CH_4 from 4 to 44%).

The isotopic composition of helium in the gas phase in the EMGW basin was studied in detail earlier (Polyak, 2005; Lavrushin, 2012). Values of $^3He/^4He$ for more than 40 samples range from ~30 to 160 ($\times 10^{-8}$). This specified that in the .» gases of mineral waters within the EMGW basin there is an insignificant amount of mantle helium ($^3He/^4He_{мант}$= 1200×10^{-8}). It confirms the genetic relationship of CO_2-phase with the Pliocene-Quaternary volcanoes of Great Caucus (Elbrus volcano).

7. BALNEOLOGICAL COMPONENTS

Mineral waters of the Essentuki area in some cases are characterized by a high content of fluorine, iodine, bromine, boric acid. A significant part of the mineral waters of the region is composed of gases. They are mainly represented by carbon dioxide, to a lesser extent of nitrogen, hydrogen sulfide, and methane. The content of CO_2 in the carbon dioxide waters for external use is normalized in the range of 1,4 g/dm^3. The composition of carbon dioxide water – HCO_3-Cl-Ca-Na and SO_4-Cl-H-CO_3 Mg-Na-Ca with TDS of 5,7-7,8 g/dm3 and concentration of free carbonic acid 1,1-1,4 g/dm^3 exploited in the Essentuki area of carbonic mineral waters. This thermal water uncovered in the Titon-Valanginian aquifer (J_{3tt}-K_{1v}), occurring at a depth of 1378 m. The water is used for the release of baths together with carbon-free waters, confined to the deposits of lower Cretaceous, in a ratio of 1:2. In recent years, the water in this mixture was called «Essentuki-new.»

The diverse composition of the Essentuki mineral groundwater area is explained by the complex hydrogeological conditions of the region. It is located in a large area and includes several aquifers with different hydrogeodynamic and hydrogeochemical conditions. In the Northern part of the EMGW area, the mineral waters are confined to the upper Cretaceous aquifer (K_2), encountered by the well at a depth of 679 m. The groundwater in the considered area is saline-alkaline, close to the «Essentuki-4» type (sodium chloride-bicarbonate), with TDS of 6.8-7.0 g/dm3, they are practically carbon-free. The gas composition is methane-nitrogen-carbon dioxide. The groundwater contains high concentrations of iodine (3.2 mg/dm^3), bromine (5 mg/dm^3), boric acid (68 mg/dm^3), and fluorine (3 mg/dm^3). In the East of the EMGW area, the mineral waters are characterized by chloride-bicarbonate sodium composition, with TDS of 2,4-2,6 g/dm3, without specific components and properties, with increased content of fluorine from 2 to 6 mg/dm^3. The water temperature at the collar of well is 28-30 °C. The water is confined to the Danish-Zeland (Elburgan) aquifer ($₽_{1d-sl}$). In the Southern part of the EMGW area, the mineral waters are confined to the upper Cretaceous aquifer (K_2) and they are carbon-free, low-salt water, bicarbonate sodium composition, with alkaline reaction, cold. The water of this composition is usually used for drinking purposes, including for industrial bottling as natural table water. Within the southwestern part of the EMGW area, the only productive carbonated mineral water is the Titon-Valanginian aquifer (J3tt-K1v), which lies directly on the Paleozoic basement. The carbon dioxide waters of hydrocarbonate type are common here as well as mixed sulfate-chloride-bicarbonate. The cationic composition of water is dominated by calcium and sodium. TDS is 6.2-7.9 g/dm^3, reaching 11.5 g/dm^3 due to the extreme saturation of water with carbon dioxide (the gas factor for the well in the initial period of the experimental release exceeded 1000 dm^3/dm^3). In the Central part of the EMGW area, the mineral waters are confined to the Danish-Zeland (Elburgan) aquifer ($₽_{1d-sl}$) and to the upper Cretaceous aquifer (K_2). The cold chloride-hydrocarbonate sodium with medium and high-salt drinking and therapeutic drinking waters «Essentuki-4» and «Essentuki-17» are confined to the Danish-Zeland (Elburgan) aquifer ($₽_{1d-sl}$). The content of carbon dioxide in waters of the «Essentuki-17» type is from 1,7 to 2 g/dm^3, TDS 11,6-12,5 g/dm^3, and pH 6,3-7,4. The water type «Essentuki-4» contain carbon dioxide in an amount of 0,67-1,1 g/dm^3, TDS from 8,2 to 8,8 g/dm^3, and pH 6,2-6,7. In the North-Central part of the Essentuki area, the upper Cretaceous aquifer (K_2) is productive on the mineral waters. As well as an aquifer of sandstones lying in the middle part of the relatively waterproof horizon, which are confined to methane high- salt (19-20 g/dm^3) sodium chloride waters with a high content of bromine (20-70 mg/dm^3), iodine (3-11 mg/dm^3), and boric acid (41-96,7 mg/dm3). The groundwater of the upper Cretaceous aquifer (K_2) by chemical composition is chloride-hydrocarbonate, «Essentuki-4» type and hydrocarbonate-chloride-type «Essentuki-17» sodium waters with TDS from 7,5-8,4 to 12,1-13,3 g/dm^3.

8. CONCLUSION

Thus, our investigation indicates that EMGW has the two-stage structure: basal complex and carbonate-terrigenous sedimentary cover with a total thickness of 1500-1800 m, declined in the north-eastern direction. The increase in the depth of layers and the removal of the recharge area consequently change the chemical and gas composition. Faults and fractured rocks surrounding them serve in the past and present time as vertical channels to fluid migration between layers and from basal complex to sedimentary cover and as lateral channels to speeding migration inside aquifers. Volcanic laccolite-peaks set also in north-eastern direction, create thermal, hydrochemical and gaseous anomalies and generate CO_2. Laccolites play an important role in the discharge of deep aquifers. Local linear, semi-circular and circular tectonic faults formed near mountains became the ways of large masses of deep groundwater to the surface. Significant stratum of Neogene clays overlays Palaeogenic and Upper-Cretaceous carbonate sediments, conserving high-salinity groundwater.

The isotope data obtained prove the meteoric origin of the mineral waters within the EMGW basin since most of the data are plot along the GLMW. The chemical composition of mineral waters mainly depends on the lithological composition of water-bearing rocks and the constituents of the gas phase. Besides, the interfacial overflows and the degree of hydrogeological openness of the horizon influence the geochemical feature of the waters. The temperature of mineral waters widely varies (10-70 °C) and strongly depends on the subsurface depth of aquifers and the local geothermal gradient (40-42 °C per km). Temperatures of waters increase in the northerly direction according to the water-bearing sediments depth.

The Essentuki mineral water basin is characterized by a wide spread of high pCO_2 sparkling Ca-Na-HCO_3-Cl waters, which are a trademark as «Essentuki 4» and «Essentuki 17», and has strong therapeutic properties. These waters are confined to upper Cretaceous and Paleogene sediments. The main therapeutic properties of these waters are due to the high concentration of Na^+ and high pCO_2. They are characterized by a high content of fluorine, iodine, bromine, boric acid.

The dominated gas of bubbling phase in almost all mineral waters within the EMGW basin is CO_2 (up to 98 vol.%) which is probably a mixture gas from deep (volcanic) and biogenic sources. However, in some mineral waters located in the central and southern parts of the EMGW basin, a high concentration of methane (up to 44 %) and nitrogen (up to 70-90%) was found. Isotopic data of $\delta^{13}C_{CH4}$ indicate the marine microbial origin of the methane phase and prove that the high methane content in the water is caused by the degradation of dispersed organic matter in the host rocks. Value of $^3He/^4He$ specified the bubbling gas in mineral waters is a mixture of several sources of gas (mantle, crustal and biogenic).

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