



Article Geochemical Characterization of Natural Groundwater on the Southern Slopes of the Caucasus Mountains on the Russian Black Sea Coast

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Abstract: The Mzymta and Sochi watersheds, located on the southern slopes of the Caucasus Mountains on Russia's Black Sea coast, are characterized by a remarkably complex geological setting. The predominant rocks are mudstones, siltstones, and shales, with smaller amounts of carbonate and clay-carbonate rocks, and occasionally igneous rocks. The area is also characterized by the occurrence of polymetallic, gold, sulfide, rare metal, and rare-earth mineralizations in addition to hosting a thermal hydrogen sulfide groundwater aquifer. The objective of this study was to determine groundwater genesis patterns in an area with such contrasting geological and hydrogeological structures. Based on the chemical analysis of 33 natural groundwater springs, five chemical types of water were identified dictated by the composition of the host rock as well as the occurrence of mineralizations, seepage of mineralized water, and local geochemical features of the host rock. The high sodium concentration and mineralization of groundwater near the thermal hydrogen sulfide groundwater aquifer are due to the infiltration of seawater. The consistent presence of excessive amounts of rare-earth elements (REEs) in all groundwaters in the area is a reflection of the regional geochemical specialization of the rocks. Groundwater, like the terrestrial components of the natural environment, inherits rare-earth fractionation patterns from the rocks that make up the area. Thus, rare-earth totals and fractionation patterns can be used as a reliable criterion to interpret the regional specificity of groundwater.

Keywords: groundwater of the Russian subtropics; chemical types of groundwater; sulfide mineralization; hydrothermal deposit and groundwater

1. Introduction

Understanding the hydrochemical processes that determine groundwater chemistry is important both theoretically and practically for predicting changes in environmental conditions. Numerous studies have been conducted around the world on factors affecting groundwater composition. A close review of these studies has identified the main factors that determine groundwater properties. The majority of researchers rate the chemical and mineralogical composition of the host rock as the primary factor. Many researchers have noted that groundwater chemistry is affected more by rock weathering than by anthropogenic interventions [1–6]. Dissolution of saline and carbonate minerals, silicate weathering, evaporation, and cation exchange are the processes that have the greatest impact on groundwater chemistry [7–10]. Chemical and mineralogical alteration of different rock types leads to the incorporation of various dissolved elements into groundwater [11–18].

Another important process is the weathering of carbonates which is associated with the precipitation of calcite and dolomite and the dissolution of gypsum [19,20]. Dissolution



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of silicate minerals, such as anorthite and labradorite, is also known to affect groundwater content [20,21]. It has been shown that in waters formed in contact with young granite, the abundance of petrogenic components and trace elements increases. Dissolution of evaporite minerals such as halite and gypsum raises total concentrations of solids and sulfates in groundwater [22].

Chemical processes such as dissolution–sedimentation, ion exchange (adsorption/ desorption), and oxidation–reduction are also known to contribute to groundwater mineralization as groundwater residence time in aquifers increases [5,18,21].

In addition, sweet groundwater chemistry in coastal marine zones may be affected by contamination from seawater intrusion into coastal aquifers [23], soil formation processes, and soil composition [24].

In studies of groundwater chemistry, it is important to take into account anthropogenic factors, which are usually associated with sewage, industrial, and agricultural effluents [25,26].

However, in the study area of the Mzymta and Sochi River basins on the Russian Black Sea coast, anthropogenic influences are almost non-existent. There is no heavy industry or large-scale agricultural production in the area. Therefore, this makes it an ideal study area for understanding the effects of geological conditions on groundwater chemistry.

The Mzymta and Sochi basins on the Russian Black Sea coast are located in the humid subtropical climate zone. The area is part of the Caucasus groundwater region, which hosts brackish, artesian, and non-artesian aquifers [27].

Although regional geology distinguishes subprovinces, regions, and subregions in the Caucasus basin, the U-shaped valleys of the Mzymta and Sochi Rivers, which are the subject of this study, have been considered without regard to this zoning. The valleys are natural drainage channels for all aquifers and formations they pass through. The main aquifer formations here are zones of major rock fracturing and cavernous porosity caused by submeridional faults.

Groundwater occurrences are typical for limestone, sandstone, marl, and clay-argillaceous rock suites in the area. The pre-Quaternary formations other than these contain little groundwater, however, and such groundwater develops only in exogenous fracture zones [27].

The area is characterized by a highly complex geological setting. Mudstones, siltstones, and shale rock suites predominate. However, carbonate rocks (limestone) and clay-carbonate rocks (marl) are also present in the middle reaches of the two rivers. Magmatic formations are locally developed only in the upper reaches of the Mzymta River. Both watersheds host various mineralizations such as polymetallic, auriferous [28], sulfide [29], rare metal, and rare-earth [30]. The region between the two watercourses hosts the Matsesta hydrothermal sulfide groundwater aquifer [31,32]. The study of groundwater chemistry and genesis patterns in an area of such complex geological and hydrogeological context is very promising for understanding the water–rock interactions.

Therefore, the objective of this study is to determine the chemical composition of groundwater in a subtropical area on the Russian Black Sea coast and to identify the relationships between hydrogeologic conditions and groundwater chemistry. The city of Sochi, a major urban agglomeration, is located in the lower reaches of the Mzymta and Sochi rivers. Although there are tourist and sports facilities in the mountainous parts of the watersheds and small settlements at the dam site, their impact on the groundwater in this area is minor and highly localized, with none of the water sources under study suffering any negative effects.

To achieve this goal, the groundwater of the Mzymta and Sochi River valleys was thoroughly investigated, focusing on rare and trace elements.

The results of this work will help to address the issue of rational use of groundwater resources in the study area and similar locations.

2. Materials and Methods

2.1. Study Area

The Mzymta River is the largest in the Greater Caucasus Mountains and the Sochi Black Sea coastal region. It originates in a small lake at an elevation of 2440 m a.s.l. and empties into the Black Sea in the Adlersky district of Sochi [33] (Figure 1). The river is 89.7 km long, with a basin area of 885 km² and a mean basin elevation of 1309 m a.s.l.



Figure 1. Geological map of the Mzymta and Sochi River valleys and groundwater outlets surveyed.

The source of the Sochi River is on the southern slope of the Greater Caucasus Mountains near the 1813-meter-high Chura Mountain [34]. The river flows into the Black Sea in the central district of Sochi. The river is 45 km long and has a basin area of 296 km². The mean annual discharge in its middle reaches about 17 m3/s and the annual fluctuations in the river level reach 2.32 m.

The upper reaches of both river valleys are U-shaped, with steep gradients of $30–35^{\circ}$, increasing to $40–50^{\circ}$ in some places. Entering the coastal lowlands, the rivers flow through wide, well-developed valleys. Both are mountainous rivers with well-defined floods in the warm season, frequent flooding in the fall, and stable low water in the winter.

The coordinates of the 33 natural groundwater outlets studied are shown in Table S1. Groundwater outlets in the river basins were surveyed from the headwaters to the mouths of the two rivers (Figure 1).

2.2. Geological Conditions

As seen on the geological map [35], the rocks of the Mzymta River valley comprise four important sections. The upper reaches are dominated by Jurassic gabbro-greenstone and granite rock suites. In the middle reaches, the valley is formed by Jurassic mudstones with bands of siltstones, sandstones, and siderites interspersed with pyrite concretions. Then the river crosses sedimentary rocks consisting of calcareous marl, marly calcareous rocks, gritstones, and sandstones. Near the river mouth, Paleogene and Neogene clays, clayey marls with siltstones, and sandstones occur at the base of modern alluvial deposits.

The upper reaches of the Sochi River valley are formed of Jurassic clay and slates. The river channel then passes across sedimentary rocks consisting primarily of mudstone and siliceous schists. Chalk limestone, sandstone, mudstone, and marl are common in the middle reaches of the river. Paleogene argillite development is found 15 km from the mouth of the river and is characterized by sandstones with marl lenses. From this point to the mouth of the river, Paleogene clays with bands of siltstone and sandstone occur at the base of modern alluvial deposits.

The two river basins are characterized by the presence of polymetallic and Au-bearing mineralizations extending over an area of tens to hundreds of square kilometers [28]. Scattered sulfide mineralizations are also numerous [29], while low and medium subalkaline rocks with specialization in rare metals and rare-earths are known to occur in the middle reaches of both rivers [30].

The area up to the middle reaches of the two rivers is part of the Caucasus Biosphere Reserve, so the anthropogenic load is minimal.

2.3. Sampling and Analysis

The subject of the study is the chemistry of groundwater from natural springs.

The geochemical characteristics of natural groundwater were established by analyzing water from 33 natural springs sampled (Figure 1).

Water sampling was conducted once during September and October 2021.

Water samples were collected in sterile polystyrene tubes.

To evaluate the cation–anion composition of the macro-elements in the water, the following parameters were measured: pH by potentiometric method [36]; dry residue by gravimetric method [37]; chlorine ion content by titration with silver nitrate solution using potassium chromate as an indicator [38]; sulfate ion content by turbidity measurement using barium chloride [39]; bicarbonate ion content by titration with methyl orange as an indicator [40]; calcium and magnesium content by trigonometric method [41]; and sodium content by Rosgidromet method of calculation [42].

The abundancies of 70 elements in groundwater were investigated by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Analyses were performed using ICP-MS-X-7, Thermo Elemental, USA. and ICP-AES-ICAP-6500, Thermo Scientific, USA. The margin of error under these methods was less than 6% compared to external standard methods [43]. Detection limits were set to nanograms per liter (ng/L) for non-prevalent elements and micrograms per liter (μ g/L) for prevalent elements.

The research was conducted at the Analytical Certificate Testing Center of the Institute of Microelectronics Technology and High Purity Materials of the Russian Academy of Sciences FSBIS (ACTC IMT RAS), Chernogolovka, Moscow Oblast.

The methodology included the following three steps: (1) ICP-AES determination of Li, B, Na, Mg, Al, P, S, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Sr, and Ba; (2) ICP-MS determination of Li, Be, B, Al, P, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Mo, Nb, Rh, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, REE, Hf, Ta, W, Re, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th,

and U; (3) Comparison of the results against two independent methods. In this step, the analytical accuracy for Li, B, Al, P, Mn, Cu, Zn, Sr, and Ba in each sample was controlled with a cross method, introducing corrections for matrix effects as necessary.

Reference samples with element concentrations ranging from 1 to 500 μ g/L were used for quality control. The method was designed to deal with spectral noise resulting from the quantification of a large number of elements due to the formation of polyatomic ions (oxides, hydroxides, hydrides, argides, etc.) in the plasma. Details can be found in [43]. Element concentrations in reference samples were determined in advance by emission spectrometry.

Mass spectral data sets were analyzed and concentrations of elements in the samples were calculated using mass spectrometer software. Li, B, Ti, Cr, Ni, Cu, Zn, Ge, Se, Br, Sr, Zr, Mo, Ag, Cd, Sn, Sb, Te, Ba, Nd, Sm, Eu, Gd, Dy, Er, Yb, Hf, W, Re, Os, Ir, Pt, Hg, Tl, and Pb concentrations were calculated as averages measured from isotopes of each metal. The limits of detection (LOD) were calculated as follows:

$$LOD = Ci + 3 \times s$$

where Ci is the average concentration of isotope i in control samples and s is the standard deviation for isotope i in control samples.

For polyisotopic elements, the LOD values for the most common isotopes were used in subsequent calculations. Relative standard deviations for all elements were not to exceed 0.3 when concentrations of these elements were measured down to $5 \times \text{LOD}$ and not to exceed 0.15 when concentrations above $5 \times \text{LOD}$ were measured.

LOD data are shown in Table S2.

To confirm the accuracy of the analyses, certified reference samples "Trace Metals in Drinking Water" by High-Purity Standards (USA) were used [44]. The data obtained were compared to the reference samples, and an average accuracy of 1–3% was ascertained.

2.4. Geochemical Characterization and Statistical Analysis of Groundwater

To compare the concentrations of chemical elements in groundwater (Ci) to the average concentrations in groundwater on a global scale (C) [45], element concentrations (Cc = Ci/C) were computed at all sampling sites. Geochemical equations were constructed by ranking chemical elements on the basis of the Cc value and binning them according to the selected intervals; elements with Cc > 1 were classified as excessive and with Cc < 1 as deficient.

To evaluate the diurnal variation in the chemical composition of the groundwater, the abundancies of chemical compounds and elements in the water samples taken in the morning and evening were calculated and their ratios established.

A factor analysis of the data was performed to identify additional patterns in the primary data set to confirm the origin of the groundwater geochemistry in the area [46,47]. The R-modification of the factor analysis using the principal components method was applied. That is, by discarding the least informative features and retaining only the most important features, the original feature space was reduced and an analysis of correlations among variables was conducted. This study was performed without specifying a priori the number of factors and their loadings.

In the factor analysis, chemical elements that were below the detection limit of the analytical method in 50% of the samples were discarded. The rare-earth element (REE) content in groundwater was replaced by the sum of light REEs (LREEs) (La, Ce, Pr, Nd), medium REEs (MREEs) (Sm, Eu, Gd, Tb, Dy), and heavy REEs (HREEs) (Ho, Er, Tm, Yb, Lu). Ultimately, factor analysis was performed with 27 components for 58 samples: Si, Ca, Mg, Al, Mn, Na, K, S, B, Rb, Sr, Li, Ba, Re, U, Sb, Cs, LREE, MREE, HREE, Y, V, Mo, Zn, Cu, Pb, and Ag. Calculations were based on the logarithmic concentrations of the elements.

The factors extracted were interpreted based on the known parameters included in the calculations as well as on the geological structure and metallogeny of the study area. Since the main cause of variance in chemical element abundance in groundwater is the elemental

diversity of the sources, the cross-interpretation of the factor analyses provided insight into the most likely sources.

Some of the factors extracted were not clearly interpretable. However, those factors accounted for only a small portion of the variance in the primary data set and were heavily influenced by local conditions of groundwater formation at a particular spring.

Of the 27 factors extracted, 6 factors were retained based on the "scree test" first proposed by Cattell [46]. Their contribution to the total variance in the primary data ranged from 4.44 to 31.75% (80.3% total). The remaining 21 factors had a contribution to variance of less than 1% (19.7% total) and were discarded.

Elements whose correlation (factor loadings) with the corresponding factor is greater than or equal to the critical value r at the 5% significance level (for n = 58) were included in the factor structure. The factor loading for an element indicates the impact of that factor on the chemical composition of groundwater.

The factor analysis first considered the loading structure of the principal factor in the unrotated coordinate system. If the result was incomplete or the individual factors were not interpretable, a varimax axis rotation was performed to obtain simpler, but more interpretable, solutions.

Factor analysis was performed using the Gold Digger software package for the integrated processing of geological and geochemical data developed at the Department of Geochemistry, Faculty of Geology, Moscow State University [48].

3. Results

3.1. Macro-Elemental Chemical Composition of Groundwater

Primary chemical composition data for the macro-elements in groundwater are shown in Table S2.

Macro-elemental analysis of groundwater in the study area identified the following five groundwater types:

- 1. bicarbonate-calcium;
- 2. bicarbonate-sulfate calcium-magnesium;
- 3. bicarbonate-sulfate calcium-sodium;
- 4. bicarbonate-chloride sodium;
- 5. bicarbonate-chloride-sulfate calcium (Figure 2 and Table 1).

Bicarbonate-calcium water is characterized by the predominance of carbonate in the anionic composition, averaging 90%. The mineralization of the water varies from 62 to 366 mg/L, with an average of 217 mg/L. The pH of the water is neutral at 7.3 units on average.

Bicarbonate-sulphate calcium-magnesium water contains mostly sulfate anions in addition to bicarbonates. The mineralization of the water ranges from 106 to 362 mg/L, with an average of 207 mg/L. The pH is neutral at 7.1 units.

Bicarbonate-sulfate calcium-sodium water is characterized by the presence of sodium cations (16%) and is slightly more acidic (6.7) than the previous two types. It is also characterized by high mineralization with an average of 633 mg/L.

Bicarbonate-chloride sodium water differs from the other water types in having the highest mineralization (1160 mg/L), a predominance of sodium in the cation composition, and high alkalinity (7.6 pH).

Bicarbonate-chloride-sulfate calcium water is characterized by a highly heterogeneous mix of predominant anions with low mineralization, averaging 322 mg/L. The pH of the water is neutral at 7.8 units.

All but one water type are characterized by the predominance of bicarbonate anions and a neutral pH, so they can be classified as soft or sweet waters [49]. The exception is the fourth type of water, which is weakly mineral and alkaline [49].



Figure 2. Piper diagram of the groundwater from the Mzymta and Sochi River valleys.

Table 1. Chemical composition of macro-elements in groundwater from the Mzymta and Sochi River valleys.

Water Type	Number of Sampling Points	Statistical Characteristics	рН	Content, mg/L						
				Mtotal, mg/L	Na ⁺	Ca ²⁺	Mg ²⁺	Cl-	SO ⁴²⁻	HCO ³⁻
I Bicarbonate calcium	29	Maximum	7.9	366.0	7.33	99.75	6.72	1.82	51.50	333.49
		Minimum	6.5	62.0	0.87	12.29	0.87	13.86	1.00	47.64
		Average	7.3 ± 0.5	217.4 ± 8.7	3.07 ± 0.2	59.31 ± 3.6	2.84 ± 0.1	6.65 ± 0.4	16.12 ± 1.1	181.63 ± 5.4
		Standard deviation	0.40	90.45	1.77	25.94	1.54	3.59	10.81	74.79
II Bicarbonate- sulphate calcium- magnesium	8	Maximum	7.75	362.0	6.37	111.3	12.78	10.50	125.0	216.16
		Minimum	6.28	106.0	1.22	13.90	1.33	2.38	40.0	51.97
		Average	7.05 ± 0.2	206.5 ± 10	4.00 ± 0.2	44.77 ± 1.3	6.32 ± 0.4	4.73 ± 0.1	76.08 ± 5.3	137.39 ± 6.9
		Standard deviation	0.48	87.5	1.90	33.55	4.13	2.80	33.37	63.25
III Bicarbonate- sulphate calcium- sodium	4	Maximum	6.80	790.0	43.50	186.6	15.26	31.22	150.0	473.0
		Minimum	6.67	574.0	37.33	151.2	7.44	10.08	130.0	368.1
		Average	6.74 ± 0.3	633.3 ± 44	39.67 ± 1.6	161.4 ± 4.8	11.68 ± 0.6	15.84 ± 0.6	141.8 ± 5.7	427.9 ± 12.8
		Standard deviation	0.06	104.7	2.74	16.95	3.22	10.27	8.88	46.44
IV Bicarbonate- chloride sodium	4	Maximum	8.10	1212	305.0	5.82	5.46	310.8	40.0	918.2
		Minimum	7.09	1104	284.0	1.76	0.21	208.8	39.0	628.0
		Average	7.58 ± 0.4	1160 ± 81	298.4 ± 15	3.61 ± 0.3	2.72 ± 0.1	275.0 ± 11	39.0 ± 2.7	754.7 ± 52.8
		Standard deviation	0.52	46.04	9.96	2.09	2.90	45.18	0.60	160.4
V Bicarbonate- chloride- sulphate calcium	4	Maximum	8.12	332.8	0.54	10.75	0.76	10.68	21.60	46.34
		Minimum	7.45	309.5	0.49	9.87	0.71	10.08	20.12	43.31
		Average	7.83 ± 0.4	322.3 ± 16	0.51 ± 0.03	10.40 ± 0.3	0.73 ± 0.1	10.45 ± 0.3	20.78 ± 0.8	45.02 ± 1.8
		Standard deviation	0.34	12.30	0.04	0.38	0.03	0.29	0.84	1.28

3.2. Groundwater Elemental Composition

Primary chemical composition data for major elements in groundwater are summarized in Table S3. Patterns revealed by the specificity analysis of chemical elements distribution in groundwater (Table S4) in comparison to their Clarke values (Table 2).

Table 2. Clarke concentrations of elements in different types of groundwater (Cc values in parenthesis).

Water Types	$Cc \ge 1$	Cc < 1
Ι	Se(7.0)-Cs(3.3)-Eu(3.0)-Tb,Ho(2.0)-Sn,Ba(1.7)- Dy(1.6)- Sr, Pr, Gd(1.4)-Ca,Nd, Sm(1.3)-Ce(1.2)-Cd,La,Er,Lu,Tm,Lu (1.0)	Zn,Yb(0.8)-B,Si(0.5)-Pb(0.4)- V,Li,Ge,Cu(0.3)- As, S, Rb, Mo, K, Al (0.2)- Hg, Br, Mg, Na,Sb,Y,Ag,U,Mn,Fe(0.1)-Th,Zr,Tl(0.01)
Π	Pr(5.4)-Se(3.2)-Tb(2.0)-Gd(1.9)-Sn(1.7) -Ba(1.3)-Cs(1.2)-Ca(1.1)-Sr,Eu,Ho,Tm,Lu(1.0)	Cd(0.7)-Si, Pb(0.6)-B,Li,Dy,Mo,La,Sm,Ce(0.4)-V,Cu,Er,Yb(0.3)- Rb,Nd,Ag(0.2)-Hg,K,Mg,Br,Na,As,Sb(0.1)- Al,U,Y,Mn,Fe,Th,Tl,Zr(0.01)
III	Ba(4.1)-Se(3.5)-Ca(3.4)-Sr(3.1)-Li(1.7)-Rb(1.3)-B(1.2)- Eu,Tb,Ho,Tm,Lu(1.0)	S(0.8)-Pr(0.7)-Si,Dy,K,Sn,Sm,Gd,Er,Cs,Ce(0.5)- Nd,Cu(0.4)-Na,V,Cd,La,Yb(0.3)-Mg,Zn(0.2)- Hg,Mn,U,Br,Mo,U,Br,Mo,Pb(0.1)- As,Al,Y,Sb,Ag,Fe,Th,Tl,Zr(0.01)
IV	Se(30.3)-Ge(21.6)-B(16.0)-Br(10.5)-Ba(7.6)-Na(6.6)- Li(4.1)-Sr(3.5)-Cr(1.3)-Mo(1.2)- Eu,Gd,Tb,Dy,Ho,Tm,Lu(1.0)	Sm,Ce,Pr(0.9)-Er(0.8)-Nd,Hg,Ni(0.7)-Ca,Cs,Si(0.6)- Yb,La(0.5)-Zn,Pb,V(0.4)-S,Rb,Cd,Cu(0.3)- K,Ag,Mn(0.2)-As,Sb,Fe,U,Al,Mg(0.1)- Y,Th,Zr,Tl(0.01)
V	Se(2.5)-Eu,Tb,Ho,Tm,Lu(1.0)	Dy,Cd,Pr(0.6)-Mo,Gd,Sn(0.5)-La,Zn,Sm,Pb(0.4)- Nd,Er,Ce,Yb,Mn,V(0.3)-Cu,Ca,Si,Ba,Hg(0.2)- B,Br,Ag,Rb,Sr,S(0.1)-As,Cs,Zr,K,Y,Al, Sb,U,Mg,Fe,Na,Th,Li,Tl(0.01)

In general, the elemental composition of groundwater is poor. Most chemical element concentrations are below their respective Clarke values. Of the 50 chemical elements analyzed, only 13 to 19 were excessive, depending on the type of water. For bicarbonate-chloride sulfate-calcium water, only six such elements were identified.

The high content of Se and rare-earth elements is a common feature of all the types of water studied. This characteristic is due to the geological conditions of the region. The clayey rocks of the area are known to be rich in these elements [50,51]. The study area is also characterized by rocks containing rare metals/rare-earths [30] and gold mineralization [28], and Se is known to be associated with the latter [52].

The first three types are also characterized by high concentrations of Ca and Sr, while deficient elements consistently comprise Al, As, Hg, Fe, Sb, Y, U, Th, and Zr.

3.3. Factor Analysis of the Elemental Composition of Groundwater

Factor analysis of chemical elements in groundwater in the study area was performed on the complete primary data set without prior sorting of water types by macro-elements; six factors (unrotated) were extracted, accounting for 80.3% (n = 58 samples, crit.5% = 0.255) of the variance in the primary data:

Factor 1—31.8% K > 0.9 Re > 0.8 (Rb, Sr, U, Li, Ba, B, S) > 0.7 (Ca, Na) > 0.6
(LREEs, MREEs, HREEs) > 0.5 (Mn, Mo, Cu, Al) > 0.4 (Y, Si) > 0.3
Ag < -0.24
Factor 2—18.2% (Y, Al, MREEs, LREEs) > 0.7 HREEs > 0.6 (Mn, Pb) > 0.4 Zn > 0.3
(Cu, V) > 0.24
(Mg, Si) < -0.5 (Li, S) < -0.4 (Cs, Sr) < -0.3 (Rb, Na,) < -0.24
Factor 3—11.0% Ca > 0.4 Y > 0.3 (HREEs, V, MREEs) > 0.24
$\overline{(Pb, Ag, Zn)} < -0.6 (Na, Cu, Mn, Sb) < -0.4 (Cs, B) < -0.3 Mo < -0.24$
Factor 4—7.8% Mo > 0.7 V > 0.6 Na > 0.4 Re > 0.3 (Sb, B) > 0.24
(Zn, Ca) < -0.4 Ba < -0.3
Factor 5—7.1% Sb > 0.7 Cs > 0.6 Mg > 0.4 Pb > 0.3 (Y, HREEs, Si) > 0.24

Factor 1 has the largest contribution to the total variance of the primary data (31.8%), reflecting the main source of the geochemical composition of groundwater in the study area. It encompasses most of the analyzed elements with their specific characteristics of solubility and mobility in the aqueous medium, pointing to the most common rock types as the principal sources of the elements in groundwater.

Factor 2, with 18.2% of the total variance, reflects the antagonistic correlation between the water content of the elements coming from mineralizations (rare-earth, polymetallics, copper, silver) [28–30], and from the petrochemical composition of the rock, including the main macro-elements Si, Ca, Mg, K, Na, and S. In other words, the higher the contribution to the total variance of elements from the mineralizations, the lower the contribution of the elements of the petro-chemical composition of the rocks.

Factor 3 accounts for 11.0% of the total variance in the primary data. Since rare-earths are correlated with Ca, a typical element in sedimentary rocks, rare-earths also had a slightly positive correlation with this factor (factor loading 0.24–0.3). Polymetals, Ag, Cu, and Sb, typical of the overlapping hydrothermal formations, had a strong negative correlation with Factor 3.

The contributions of Factors 4 and 5 to the total variance of the primary data were low and close: 7.8% and 7.1%, respectively. There is no cohesive interpretation of the variables related to positive or negative factor loadings for these factors. Varimax axial rotation did not provide a better understanding of the processes governing elemental ingress into the groundwater. This may be due to the very localized petrochemical and geochemical composition of the rocks that supply the springs under study.

Factor 6, which accounted for only 4.4% of the total variance, contributed little to the groundwater composition and its variables had very low factor loadings.

4. Discussion

4.1. Macro-Elemental Chemical Composition of Groundwater

Most of the area is characterized by groundwater of the hydrocarbon-calcium type, trapped in carbonate rocks that extend into the middle reaches of the Mzymta and Sochi rivers. Occasionally, these groundwaters are also found in argillites and sandstones with siltstone streaks, which may be related to the development of lenses and limestone interbeds in these sedimentary rock suites.

A deep erosional trench in the upper reaches of the Mzymta River has probably tapped the local water-bearing horizons associated with the limestone bands. This would explain the heterogeneity of groundwater chemistry westward in the study area from the mouth of the Tikhaya River downstream on the right bank of the Mzymta River (Figure 1).

In general, the bicarbonate-sulfate calcium-magnesium type water is typical in areas dominated by mudstones, siltstones, and sandstones [35]. Springs with this type of water are most common in the upper and middle reaches of the Mzymta River. Sulfate anions are predominant in these springs because of the sulfide mineralization zones scattered throughout the area.

Polymetallic and sulfide-auriferous mineralizations are quite typical for the two river basins and can span tens to hundreds of square kilometers [35]. In the area of interest, such zones extend from southeast to northwest (Figure 1).

In general, the regional hydrochemical speciation is determined by two typomorphic groundwater types: bicarbonate-calcium and bicarbonate-calcium sulfate. The composition of the first type is attributed to the makeup of the host rock. The second is due to the presence of overlying zones of sulfide mineralization.

The other three water types are a lot less common, and their chemistry is dictated by various local factors.

Bicarbonate-sulfate calcium-sodium water occurs between the valleys of the Mzymta and Sochi rivers in the middle reaches of the Matsesta River (Progress Springs, Figure 1). This water differs from other springs in the area in the composition of predominant cations, with an average of three times higher mineralization and an order of magnitude higher Na content.

This can be explained by the proximity of the Matsesta hydrothermal hydrogen sulfide aquifer, the true boundaries of which have never been established. According to the chemical composition of the water, the aquifer belongs to the sodium thermo-chloride-sulfide type and is rich in free hydrogen sulfide [31]. The deposit has been explored from the Mamayka River to the Kudepsta River on the Black Sea coast, in an area of about 160 km² and at a depth of 2.5–3.3 km. The occurrence and distribution of Matsesta-type hydrosulfide springs in the area are typical of fractured karst limestones.

What is interesting is that its karst system is closely connected not only with the atmospheric recharge zones, but also by diffusion with the sea, and receives both fresh water and seawater in a constant hydrodynamic equilibrium [32].

The chemistry of the bicarbonate-sulfate type water indicates that it originated under the influence of the Matsesta aquifer. The high sodium concentration and high degree of mineralization are similar to the chemical specificity of mineral springs in aquifers partially recharged from the sea.

The bicarbonate-chloride-sodium type water occurring in the upper reaches of the Khosta River differs from all other water types in that it is highly mineralized and alkaline [49]. The water is not suitable for drinking, as its total mineralization exceeds the MAC by 1.2 times. There is no obvious explanation for the increased salinity, but it is likely related to the proximity of the site to the source of the salinity and the presence of mercury mineralization (Figure 1).

The compositional features of the bicarbonate-chloride-sulfate groundwater in the upper reaches of the Mzymta River are attributed to its development in igneous rocks, which distinguishes this region from the other sites under study. The contrasting composition of the igneous rocks (gabbro-greenstones and granites) dictates the heterogeneous nature of anions in this water.

Note that sodium is the predominant cation in two of the five water types analyzed. Sodium enters natural waters primarily through the dissolution of substances during plagioclase feldspar weathering. Clay minerals are also known to provide abundant exchangeable sodium under certain conditions [51].

Host rock composition also explains the relatively high content of calcium and strontium in the second water type. Sedimentary rocks widely distributed in the area are known to be richer in these elements than other types of rocks [50]. This is confirmed by the absence of Ca and Sr among the excess elements in groundwater that occurs in the upper reaches of the Mzymta River, where magmatic rocks predominate.

4.2. Groundwater Elemental Composition

Most interesting is the presence of trace elements in the region's groundwater, as their nomenclature reflects the nature of mineral sources and their impact on the groundwater.

The consistent presence of REEs among excess chemical elements in the groundwater of the area is due to the regional geological setting. Clay rock suites in the area are known to be enriched in REEs [51]. The role of clay rocks as a source of elevated REE concentrations in groundwater is confirmed by the close correlation of REEs with aluminum (r = 0.988 with r 5% crit. = 0.278), one of the most typomorphic elements of clay rocks. In addition, the middle reaches of the rivers of the region are known to host suites of low and medium subalkaline rocks with specialization in rare metals and rare-earths [30].

The behavior of REEs in groundwater is of particular interest as a means of assessing interaction patterns within the water–host rock system. Because of their uniform chemical properties, REEs exhibit similar behavior when involved in natural processes, with the result that groundwater inherits fractionation patterns of REEs that are characteristic of specific rock suites. As the rock changes, the proportions of individual elements or groups of elements also change, affecting the REE fractions in groundwater [53,54].

The highest REE content was found in the first type of groundwater in basins composed primarily of sedimentary carbonate rocks that have the highest REE concentrations in the area. Rare-earth totals in this water type are, on average, 2.6 times higher than in other water types.

By analogy with [53], the elements were classified into light REEs (La, Ce, Pr, Nd), medium REEs (Sm, Eu Gd, Tb, Dy,) and heavy REEs (Ho, Er, Tm, Yb, Lu, Y) to reflect the relative positioning between the elements.

Rare-earth element concentration spectra normalized to the North American Shale Composite (NASC) [53,54] show that all groundwater types are systematically enriched in medium rare-earth elements (MREEs), which indicates REE fractionation (Figure 3).



Figure 3. REE concentration spectra normalized to the North American Shale Composite (NASC) [53,54] and total REEs in various groundwater types.

Similar fractionation patterns of rare-earth elements were found in both bedrock and channel sediments [27] in the study area. The chemical composition of sediments at any point in the channel is considered a natural average sample of the rocks of the denudation basin [52]. In other words, groundwater and sediments inherit the rare-earth fractionation patterns of the rocks that make up the area. In addition, similar REE fractionation patterns were also found in surface water, soil, vegetation, [51] and even in the soft tissues of the Mediterranean mussel [55] in the coastal area near the mouth of the Mzymta River.

The second water type is the most striking example of the regional specificity of rare-earth fractionation patterns.

The values of rare-earth elements and the nature of their fractionation can be used as alternative structural features to interpret the regional characteristics of groundwater.

Factor analysis of the raw data on the content of various chemical elements in groundwater identified their principal sources, which were then hierarchically ordered from general to specific.

The most significant contribution to the diversity of the chemical composition of all types of water comes from the rocks that filter and contain groundwater. The minerals derived from these rocks allow water to be classified into different types according to its elemental contents.

The second most important factor is the presence of ore mineralization, seepage of mineralized water, and specific geochemical features of the rocks in the groundwater basin. Mineral outcrops contribute significantly to the elemental composition of groundwater,

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especially its share of trace elements, and antagonize the elemental sources derived from the rock.

Inside this mineralization factor, there are actually two antagonistic sources of elements: ore outcrops supplying REEs to groundwater and ore outcrops supplying polymetals, Ag, Cu, and Sb. Their antagonism is likely related to the spatial separation between the outcrops supplying different elements.

The positive relationship of Mo, Cu, U, and S with Factor 6 suggests that a small amount of groundwater is formed under the weak influence (given the low concentrations) of sulfide copper-molybdenum and uranium mineralizations.

It should be noted that the choice and order of chemical elements in all the factors extracted do not reflect their water mobility [56].

5. Conclusions

Based on the study of groundwater chemistry in 33 natural springs, five water types were established: (1) bicarbonate calcium; (2) bicarbonate-sulphate calcium-magnesium; (3) bicarbonate-sulphate calcium-sodium; (4) bicarbonate-chloride sodium; and (5) bicarbonate-chloride-sulphate calcium. Bicarbonate calcium water is abundant in areas where carbonate rocks predominate. Bicarbonate-sulphate calcium-magnesium water is common in clay formations, and its genesis is associated with zones of sulfide mineralization. The occurrence in the study area of bicarbonate-sulfate calcium-sodium water is linked to the presence of the hydrogen sulfide hydrothermal aquifer, which is connected to the sea by diffusion. Localized occurrence of mineralized bicarbonate-chloride-sodium water is common in areas of mercury mineralization. Highly heterogenous magmatic rocks determine the mixed nature of anions in the bicarbonate-chloride-sulfate calcium water.

The analysis of the relative abundances of chemical elements in the groundwater of the area compared to their Clarke values revealed low abundances of most chemical elements. In most water types, only 13 to 19 of the 50 chemical elements analyzed were detected in meaningful concentrations, while in bicarbonate-chloride-sulphate calcium water, only 6 of these elements were found. However, all types of water were characterized by high Se and rare-earth element concentrations. This characteristic is attributed to the composition of clay rocks in the area, which are known to be enriched in these elements. In addition, bicarbonate calcium, bicarbonate-sulphate calcium, and bicarbonate-sulphatecalcium sodium types of water were characterized by excess Ca and Sr concentrations. The elements with consistently low concentrations were: Al, As, Hg, Fe, Sb, Y, U, Th, Zr, and Th.

Factor analysis of the abundance ratios of 70 chemical elements shows that elements derived from the host rock make the greatest contribution to the diversity of groundwater chemistry. Next are spatially separated ore mineralizations, seepage of mineralized water, and localized geochemical features of the host rock. Little correlation was found between concentrations of chemical elements in groundwater and their mobility patterns in the aquatic environment.

To the extent that the results of this study predict the chemical composition of groundwater in an area of known geological structure, they can be used to plan the rational use of groundwater resources in that area, as well as in other similar areas.

The study's finding that groundwater geochemistry reflects the occurrence of ore mineralizations in the investigated hydrogeologic basin can be used to plan and carry out hydrochemical prospecting for mineral resources.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/w14142170/s1, Table S1: Outlet coordinates, designations, and numbers on map; Table S2: Chemical composition of groundwater of the Mzymta and Sochi River valleys; Table S3: Elemental composition of groundwater of the Mzymta and Sochi River valleys; Table S4: Average chemical element concentrations in groundwater and groundwater clarks by [40], µg/L (P, Sc, Ti, Co, Nb, Ru, Rh, Pd, Te, Tm, Lu, Hf, Ta, W, Os, Ir, Pt, and Au are below analytical detection limits). **Author Contributions:** Conceptualization, and methodology, L.Z.; software; validation, Y.L., A.R.; formal analysis, R.S.; investigation; resources, S.S. and G.V.; data curation, L.Z.; writing—original draft preparation, L.Z., Y.L.; writing—review and editing, L.Z., Y.L., R.S.; visualization, L.Z., Y.L.; supervision S.S. and G.V.; project administration, S.S. and G.V.; funding acquisition, S.S., A.R., L.Z. All authors have read and agreed to the published version of the manuscript.

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