Study of Indicator Properties of Chemical Elements, Corresponding to Geochemical Environment of Natural Mineral Water Formation

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Abstract. Studies show that unique hydro-chemical indicators that meet the spatial patterns of geochemical environments characterize each land area. The authors proposed a method to study the regularities in the chemical composition of natural mineral waters and identify the indicator elements that correspond geochemical peculiarities of their formation. The initial material of the study included the results of the water chemical analysis conducted on the mass spectrometer with inductively coupled plasma (ISP-MS) Elan 9000 DRC II (Perkin-Elmer, USA). Mineral waters were characterized by a set of qualitative and quantitative parameters: geochemistry of water migrants, element-by-element comparative analysis of the concentrations, areas of origin and the water extraction conditions. These parameters are linked in the summary table, from which a number of regularities were established. The following indicator elements are identified: Sr, Ba, Mn, Li, Br, B, I, Ge, Rb, corresponding to geochemical parameters of water formation environment.

Keywords: mineral waters, geochemistry of environments, chemical composition, indicators, formation of water.
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Introduction

The chemical composition of groundwater, including mineral water, is a consequence of the interaction of geological rocks with underground hydrosphere, where water as a universal solvent is the main agent of water removal from mineral migrants (Perelman, 1982; Shvartsev, 1998). Specific hydrochemical indicators, acting as regional indicators of groundwater origin, characterize each land area. As our research shows, each of the natural mineral water is characterized by its 'fingerprint' of content and set of chemical elements, which act as 'geographic markers' for origin of water (Amelin et al., 2012). In addition to the practical significance, which is established in the falsification and geographical origin of natural mineral waters, study of chemical composition of water focuses on other tasks, one of which is reduced to the establishment of relationships between the chemical composition of natural mineral waters and geochemistry of their formation.

The purpose of this work is to study regularities in the chemical composition of natural mineral waters, and identify elements-indicators that meet the geochemical features of their formation.

Experimental part

We used a quadrupole mass spectrometer with inductively coupled plasma (ICP-MS) "Elan 9000 DRCII" (Perkin-Elmer, USA). The data were processed by a computer program "Elan ICP-MS Instrument Control ver. 3.4" (Perkin-Elmer, USA).

As standards we used certified 1g/l mono- (K, Mg, Ca, Zn, Fe, Na) (Panreac, Spain) and multi-element solutions for ICP-MS (Perkin-Elmer, USA). The dilutions were carried out in a plastic dish by ultrapure deionized water 15-18 MOhm-cm^2 (TU 2123-002-00213546-2004). For the preparation of samples and blank samples we used concentrated nitric acid "ACS" (GOST 11125-84). The calibration solutions were prepared by diluting the appropriate standards. To review the analysis and identify mineral waters we used semiquantitative "TotalQuant" data collection mode, the advantage of which is in determination of the total isotope elemental composition of the sample in a relatively short measuring time (2-3 min).

Object of research

We investigated the following natural mineral waters: Narzan, Yessentuki number 17, Essentuki number 4, Rychal-Su, Perrier, Vitasnella, Livissima, Serebrany Sokol, Suzdalsky napitki, Lipetsky Byuvet. The initial materials of study were the results of a multi-element analysis and content of the major macro-ingredients (Table 1.2). The analysis was conducted on the data basis of FSBI "Federal Centre for Animal Health" in the framework of the identification of mineral waters, purchased in an open market, by geographical origin. The database was created based on waters of the relevant sources or wells.

Results and discussion

On the basis of a comprehensive approach the authors proposed a method to identify the indicator properties of some chemical elements that emphasize the geochemical characteristics of media formation of natural mineral waters. Mineral waters have been characterized by the following set of parameters: geochemistry of water migrants, element-wise comparative analysis of the concentration, areas of origin and water extraction conditions. The above set of parameters is configured in the summary table.

Geochemical properties of water migrants

The migration properties of most chemical elements are studied fully and are the criteria for geochemical classification,

Detected element (PO*, mcg/L)	Narzan (glass plastic)	Essentuki No. 17 (glass plastic	Essentuki No. 4	Rychal-Su (glass plastic	Serebrany sokol (plastic	Suzdalskiye napitki (plastic	Lipetsky Byuvet (plastic	Vitasnella (plastic)	Livissima (plastic)	Perrier (glass)
Li (0,1)	140 150	1010 990	1100	1600 1500	9,5	3,8	160	1,5	2,0	7,6
Be (0,1)	0,042 0,031	0,021 **-	-	0,37 0,27	-	-	0,011	-	-	-
B (1)	400 420	5900 5800	6600	4400 4500	7,7	3,6	3300	10	36	51
Al (0,1)	1,2 1,7	2,9 3,1	5,2	4,9 3,3	5,6	4,8	3,8	3,0	4,6	7,4
P (10)	21 15	29 30	25	38 64	346	550	0,23	0,14	0,18	10
Sc (1)	4,5 4,7	5,3 5,8	3,9	13 14	5,9	6,4	1,9	2,2	1,4	3,5
Mn (0,1)	120 110	30 20	8,4	15 17	0,26	0,40	59	0,35	0,62	0,18
Co (0,05)	0,22 0,12	0,11 0,092	0,12	0,23 0,20	0,032	0,032	0,18	0,086	0,038	0,15
Ni (0,1)	4,1 3,8	2,5 2,9	3,1	1,8 2,1	3,0	1,3	2,1	1,6	0,77	1,0
Cu (0,05)	3,1 3,5	2,1 1,8	3,7	2,2 1,9	0,71	0,81	9,5	0,52	0,32	3,6
Ge (0,1)	0,18 0,20	6,7 6,1	13	53 56	0,042	0,058	0,051	0,018	0,0006	0,015
Br (10)	1250 1280	13500 14000	13700	3800 3850	35	38	7100	0,012	18	190
Rb (0,05)	9,0 11	16 15	18	20 26	1,8	1,1	2,5	0,02	0,21	1,2
Sr (0,05)	12000 11000	10600 9100	4400	2300 2400	134	85	1700	2000	51	960
Y (0,05)	0,048 0,052	0,081 0,087	0,045	0,097 0,091	0,0004	0,0004	0,0014	0,011	0,023	0,0023
Zr (0,05)	0,20 0,16	2,3 1,7	1,3	1,5 1,3	0,0055	0,0009	0,0007	0,076	0,0095	0,042
Mo (0,1)	4,8 3,8	0,68 0,59	0,084	0,030 0,029	1,5	0,38	0,60	0,95	0,94	2,7
Rh (0,05)	0,68 0,63	0,56 0,32	0,14	0,11 0,10	0,0071	0,0003	0,059	0,16	-	0,027
Ag (0,05)	14 60	0,94 0,13	0,29	0,0007 -	0,0044	120	0,0007	0,0023	0,0031	0,0008
Cd (0,05)	0,0035 0,0043	0,0011 0,0009	0,010	0,0009	0,0071	0,011	0,0008	0,0080	0,0081	0,0009
Sb (0,05)	- 0,36	0,012 0,15	0,012	0,011 0,22	0,33	0,40	0,42	0,61	0,63	0,075
Te (0,05)	0,012 0,013	0,069 0,060	0,069	0,043 -	0,013	-	0,059	0,0050	0,024	-
I (5)	390 480	15000 13000	9900 8900	900 880	37	15	590	110	480	20
Cs (0,05)	2,0 2,4	1,1 1,0	0,97 0,85	0,10 0,081	0,21	0,22	0,087	0,38	0,26	0,0065
Ba (0,05)	11 12	1400 1300	2060	2500 2600	0,17	0,25	6,5	44	5,7	38
La (0,05)	0,0015 0,0011	0,016 0,012	0,024	0,017 0,015	0,0035	0,0031	0,0013	0,0022	0,021	0,0047
Ce (0,05)	0,013 0,0004	0,0052 -	0,0055	0,018 -	0,0065	0,0021	0,0005	0,0039	0,0046	0,024
Eu (0,05)	0,0027 0,0035	0,21 0,18	0,31	0,44 0,45	0,0008	0,0007	0,0003	0,0049	0,0005	0,0099
W (0,05)	0,0169 -	0,36 0,35	0,14	0,14 0,17	0,018	0,047	0,0049	0,02	0,11	0,075
Tl (0,05)	0,84 0,73	0,0020 0,0010	0,0021	- -	0,0005	-	-	-	-	-
Pb (0,05)	0,95 0,93	0,35 0,40	0,045	0,11 0,099	0,18	0,85	0,68	0,049	0,010	0,28
Bi (0,05)	0,46 0,32	0,20 0,15	0,047	0,010 0,0089	0,39	0,077	0,0035	0,0092	0,0051	0,0082
Th (0,05)	0,0022 0,0025	0,021 0,016	0,0076	0,014 0,016	0,0019	0,0019	0,018	0,0007	0,0009	0,0010
U (0,05)	2,4 2,7	0,45 0,43	0,0048	0,020 0,014	1,1	0,32	0,11	6,5	5,0	3,9

*Table 1. The results of the review analysis of natural mineral water (mcg/L, average value of three different batches of water). Note – *PO – the detection limit, **– not detected.*

Mineral water	Cl^-	SO_4^{2-}	HCO_3^-	Ca^{2+}
Suzdalskiye napitki	5-7	8-15	130-160	30-45
Serebrany sokol	<10	<25	200-300	35-70
Lipetsky Byuvet	500-850	1200-1700	200-400	120
Levissima	0,3	13,7	56,8	19,5
Perrier	25	48	445	158
Vitasnella	1,3	80	296	82
Narzan	100-150	300-500	1000-1500	300-400
Rychal-Su	450-550	<25	2500-3000	<25
Essentuki No. 17	1400-2100	<25	5200-6500	<100
Essentuki No. 4	1500-1900	<25	3600-4500	<150

Table 2. The content of basic macro-ingredients of mineral water (mg/L, average value of three different batches of water).

Element	*c*, mcg/L	c_{max}/c_{min}	Element	*c*, mcg/L	c_{max}/c_{min}
Li	1,5-1600	1066	B	3,6-6600	1833
Br	0,012-14000	116666	Sr	51-12000	235
I	15-15000	1000	Ba	0,17-2600	15294
Al	1,2-7,4	6	Ni	0,77-4,1	5,3
Mn	0,18-120	667	Ge	0,0006-56	93333,3
Cu	0,32-3,7	11,56	Mo	0,029-4,8	165,5
Rb	0,02-26	1300	U	0,11-6,5	59
Cs	0,0065-2,4	369			

Table 3. The concentration ranges and value c_{max}/c_{min} for elements in studied mineral waters.

which makes it possible to trace the path of their introduction into the mineral water solutions (Kraynov et al., 2004). At the same time, water migration of such elements as W, Y, Rh, Te, La, Eu, Ce is poorly studied, especially as the concentration of these elements is less than 1mcg /L, along with elements such as Co, Pb, Tl , Th, Zr.

Element-wise comparative analysis of concentrations

In the analysis we used the most informative values: 1) the range of concentrations; 2) ratio of the maximum to the minimum concentrations (c_{max}/c_{min}, Table 3).

The value of cmax/cmin for elements Sr, Ba, Mn, Li, Br, B, I, Ge, Mo, Rb, Cs is measured in hundreds and thousands of times. Concentrations of Mo, Cu, Cs are less 5 mcg/L, which is negligible as compared with other elements. Lets express the value of element concentration in percentage and arrange mineral water in order to increase their concentration (Table 4).

Areas of mineral waters origin

Extraction of water under investigation is carried out both on platform and mountain areas:

1) Water from the platform area of the East European Plain (Serebrany sokol, Suzdalskiye napitki, Lipetsky Byuvet);

2) Water from mountain area of the Alpine region (Levissima, Perrier, Vitasnella) and the Caucasus (Narzan, Rychal-Su, Essentuki number 17, Essentuki number 4).

Water extraction conditions

Information about the method of mineral water extraction and temperature conditions is presented in Table 5.

1	Vitasnella 0,077	Levissima 0,42	Serebrany sokol 0,22	Perrier 0,15	Vitasnella 0,094	Vitasnella 0,000087	Suzdalskiye napitki 0,054	Suzdalskiye napitki 0,1	Levissima 0,0011
2	Levissima 0,81	Suzdalskiye napitki 0,71	Suzdalskiye napitki 0,01	Serebrany sokol 0,22	Levissima 0,125	Levissima 0,13	Serebrany sokol 0,12	Perrier 0,13	Perrier 0,028
3	Suzdalskiye napitki 4,23	Serebrany sokol 1,12	Levissima 0,28	Vitasnella 0,29	Suzdalskiye napitki 0,24	Serebrany sokol 0,25	Vitasnella 0,15	Serebrany sokol 0,12	Vitasnella 0,34
4	Perrier 4,61	Perrier 8	Lipetsky Byuvet 0,26	Suzdalskiye napitki 0,33	Perrier 0,47	Suzdalskiye napitki 0,28	Levissima 0,54	Vitasnella 0,73	Serebrany sokol 0,79
5	Serebrany sokol 6,92	Lipetsky Byuvet 14,17	Narzan 0,44	Levissima 0,51	Serebrany sokol 0,59	Perrier 1,38	Perrier 0,77	Narzan 2,6	Lipetsky Byuvet 0,096
6	Lipetsky Byuvet 9,61	Vitasnella 16,67	Perrier 1,52	Essentuki No. 4 7	Narzan 8,75	Narzan 9,12	Narzan 6,06	Levissima 3,2	Suzdalskiye napitki 0,11
7	Narzan 42,31	Rychal-Su 19,17	Vitasnella 1,76	Rychal-Su 12,5	Lipetsky Byuvet 10	Rychal-Su 27,74	Lipetsky Byuvet 50	Lipetsky Byuvet 3,93	Narzan 0,34
8	Essentuki No. 17 61,54	Essentuki No. 4 36,67	Essentuki No. 17 56	Essentuki No. 17 25	Essentuki No. 17 63,12	Lipetsky Byuvet 51,82	Rychal-Su 66,66	Rychal-Su 6	Essentuki No. 17 12,64
9	Essentuki No. 4 69,23	Essentuki No. 17 88,33	Essentuki No. 4 82,4	Lipetsky Byuvet 49,17	Essentuki No. 4 68,75	Essentuki No. 17 98,54	Essentuki No. 17 89,39	Essentuki No. 4 66	Essentuki No. 4 24,53
10	Rychal-Su 100	Narzan 100	Rychal-Su 100	Narzan 100	Rychal-Su 100	Essentuki No. 4 100	Essentuki No. 4 100	Essentuki No. 17 100	Rychal-Su 100

Table 4. The distribution of mineral water by increase of concentration % in mineral water for Rb, Sr, Ba, Mn, N, Br, B, I, Ge.

The layout of summary table

To identify regularities, the set of parameters is configured in the table 6.

Qualitative parameters:

1) Horizontal line – number of microelements differentiated by properties in aqueous solutions (anions and cations) and by mobility;

2) Vertical line – number of mineral water, grouped on areas of origin – platform (P) or Mountain (G);

3) Method of production – source (Is) or well (Sk, depth);

4) Temperature mode – non-thermal (0), weakly thermal (t), thermal (T).

Quantitative parameters:

5) Values of concentrations of selected items in %, positions in the row;

6) Ranges of element concentrations (mcg/L) and cmax/cmin;

7) Content of macro-ingredients Cl^-, $SO4^{2-}$, $HCO3^-$, Ca^{2+} (mg/L)

Mineral water	Mineral water extraction	Temperature conditions
Suzdalskiye napitki	source	non-thermal
Serebrany sokol	well, depth 60 m	non-thermal
Lipetsky Byuvet	well, depth 106 m	non-thermal
Levissima	source	non-thermal
Perrier,	source	non-thermal
Vitasnella	source	weakly thermal
Narzan	source	weakly thermal
Rychal-Su	source	weakly thermal
Essentuki No. 17	well, depth 685,8 m	thermal
Essentuki No. 4	well, depth 865 m	thermal

Table 5. The method of extraction and temperature mode of mineral water.

We set the following statements as the result of handling the sum of parameters in the table within the causal chain:

1. High concentrations of bromine, boron and iodine are characteristic of well waters of the Caucasus region, which indicates the presence of boron and iodine-bromine waters, confined to a negative geological structures – troughs of foothill areas. These structures accumulate brine (sodium chloride water) – the most favorable conditions for the accumulation of anions. High concentrations of bromine and boron in Lipetsky Byuvet are due to the inflow of deep brines from the area of stagnant water exchange in the overlying artesian basins.

2. Accumulation of germanium goes in sulfosalts formed under hydrothermal conditions in the surface, shallow, less medium depths that explains waters position relative to each other. First place is given to source of

Mineral water, qualitative parameters			macro-ingredients				microelements								
							anions				cations				
							Br	**I**	**B**	**Ge**	**Rb**	**Li**	**Ba**	**Sr**	**Mn**
							Very Mobile		Mobile	Poorly-Mobile				Mobile	
			Cl^-	SO_4^{2-}	HCO_3^-	Ca^{2+}	**0,012-14000 116666**	**15-15000 1500**	**3,6-6600 1833**	**0,0006-56 93333,3**	**0,02-26 1300**	**1,5-1600 1066**	**0,17-2600 15294**	**51-12000 235**	**0,18-120 667**
Suzdalskiye napitki			5-7	8-15	130-160	30-45	0,28	0,1	0,054	0,109	4,23	0,24	0,01	0,71	0,33
P	Is	0					4	1	1	6	3	3	2	2	4
Serebrany sokol			<10	<25	200-300	35-70	0,25	0,24	0,12	0,079	6,92	0,59	0,0068	1,12	0,22
P	Sk 60	0					3	3	2	4	5	5	1	3	4
Lipetsky Byuvet			500-850	1200-1700	200-400	120	51,82	3,93	50	0,096	9,61	10	0,26	14,17	49,17
P	Sk 106	0					8	7	7	5	6	7	4	5	9
Livissima			0,3	13,7	56,8	19,5	0,13	3,2	0,54	0,00113	0,81	0,125	0,23	0,42	0,51
P	Is	0					2	6	4	1	2	2	3	1	5
Vitasnella			1,3	80	296	82	0,000087	0,73	0,15	0,034	0,077	0,094	1,76	16,67	0,29
G	Is	T					1	4	3	3	1	1	7	6	3
Perrier			25	48	445	158	1,38	0,13	0,77	0,028	4,61	0,47	1,52	8	0,15
G	Is	t					5	2	5	2	4	4	6	4	1
Narzan			100-150	300-500	1000-1500	300-400	9,12	2,6	6,06	0,34	42,31	8,75	0,44	100	100
G	Is	t					6	5	6	7	7	6	5	10	10
Rychal-Su			450-550	<25	2500-3000	<25	27,74	6	66,66	100	100	100	100	19,17	12,5
G	Is	t					7	8	8	10	10	10	10	7	7
Essentuki No. 17			1400-2100	<25	5200-6500	<100	98,54	100	89,39	12,64	61,54	63,12	56	88,33	25
G	Sk 685	T					9	10	9	8	8	8	8	9	8
Essentuki No. 4			1500-1900	<25	3600-4500	<150	100	66	100	24,53	69,23	68,75	82,4	36,67	7
G	Sk 865	T					10	9	10	9	9	9	9	8	6

Table 6. Summary of quantitative and qualitative parameters.

Rychal-Su and the thermal waters of Caucasus, followed by water from the platform region and then alpine water. The last in the chain is non-thermal open source Livissima with a negligible concentration of germanium 0.00113%.

3. Lithium and Rubidium are satellites of active geodynamic processes. Rubidium is found in acid igneous rocks. It personifies the type of igneous rocks – granites and pegmatites, serving as lithological basis of waters extraction point. Comparison of lithium and rubidium concentrations in the waters of the alpine regions and the Caucasus underscores the differences of formation conditions, possibly related to the speed of water exchange. Much of the lithium concentration in the Lipetsky Byuvet confirms fluid connection with the waters of stagnant regime, carried on deep faults.

4. The concentrations of barium and its precipitant SO_4^{2-} are correlated. When contacting the deep non-sulfate waters of chlorite hydrocarbonate composition with infiltration waters, a sulfate barrier arises and barite is precipitated. With increasing depth, miscibility decreases; hence the concentration of barium increases with the depth of water exctraction. Thus, barium can serve as the indicator of the miscibility degree of non-sulfate waters with infiltration waters. Narzan shows a low concentration of barium. Probably, it is connected with enrichment of glacial melt waters. Water Rychal-Su, on the other hand, shows the maximum concentration not only in barium, but also in germanium, rubidium and lithium, suggesting that non-sulfate water does not meet on its way geochemical barriers for thesr elements, directly discharging in the source.

5. By geochemical properties strontium is analogue of barium and calcium. In the first case, strontium content is controlled by sulphat, so deep chloride waters are rich in it (Essentuki number 17, Essentuki number 4, Lipetsky Byuvet). Waters of the Alpine region are arranged in series in the temperature regime for barium and strontium. In the second case the strontium and calcium contents are correlated as shown by the example of Narzan. Apparently, an active leaching by glacial melt waters of igneous (granodiorite and diorite) and sedimentary rocks based on calcite (limestone of the Jurassic and Cretaceous) dissolves calcium and contained in them celestite ($SrSO_4$).

6. Low concentrations of manganese are typical for waters Suzdalskye Napitki and Serebrany Sokol, which is a consequence of the high content of dissolved oxygen; a similar situation with waters of the Alpine region. A different situation is with the waters of the Caucasus region: Essentuki number 4, Essentuki number 17 and Rychal-Su are characterized by relatively low concentrations of manganese – the presence of hydrogen sulfide in the hydrogeological systems. Mineral water Narzan shows the maximum concentration of manganese, regardless of the high degree of dilution by melt water, which is associated with the manganese mineralization area. Process of manganese migration is possible from igneous rocks in limestone that make up the lithological basis of extraction area, then its accumulation in carbonate rocks, followed by the removal by aqueous solutions from rocks by analogy with strontium. The high concentration of manganese in the Lipetsky Byuvet underlines the transport function of the ancient faults inherent in the element migration from the deep geological structures into the upper strata.

Conclusions

The method proposed by the authors on the basis of a comprehensive approach integrates qualitative and quantitative parameters in a single table. This form of the material arrangement allows us to make a causal chain and establish a number of important regularities. The regularities of macro-ingredients are identified between content and trace elements in conjunction with the factors of the formation of natural mineral waters. The study confirmed the indicator properties of elements Br, I, In, Ge, Rb, Li, Ba, Sr, Mn, corresponding geochemistry environments of formation waters.

Conclusions based on the summary table, made by the authors serve as preliminary findings, as the range of investigated mineral waters does not exceed ten items. For more accurate findings more statistical data is required, therefore the established regularities for the indicator properties of each element are in the order of discussion.

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