

Background contents of some minor and trace elements in the rocks on Bulgarian territory

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Ю. Христова, Д. Христов, С. Куйкин – Фоновые содержания второстепенных и редких элементов в горных породах Болгарии. Вычислены справочные значения средних фоновых (нормальных) содержаний и верхние граничные значения фонового содержания второстепенных и редких элементов (Be, Sr, Ba, Sc, Ti, V, Cr, Mo, W, Mn, Co, Ni, Cu, Zn, Cd, Hg, Sn, Pb и As) в неизмененных магматических, метаморфических и осадочных породах. Данные об их концентрации и распределении выявлены путем обобщения и статистической обработки результатов, полученных при геохимических исследованиях в Болгарии, проведенных в периоде 1960–2003 г. Массив данных состоит из 19 443 количественных или приближенно-количественных определений перечисленных элементов в 2589 пробах — представительных для комплексов разного возраста и геологического положения. Определялись средние содержания элементов, их рассеивание, верхние граничные значения и т.д. Установлена специфичность перечисленных параметров в разных типах пород. Для некоторых элементов характерна значительная геохимическая дифференциация в зависимости от типа пород. Самую интенсивную дифференциацию показывают Ti, Cr, Ni и Hg. Ультраосновные и основные породы отличаются высокими содержаниями Ti, V, Cr, Ni, Co и Mn. Самые высокие концентрации Be и Pb установлены в кислых и умеренокислых породах. Получены средние содержания элементов (в ppm) для всех типов пород: Be — 2, Sr — 280, Ba — 506, Sc — 9, Ti — 2956, V — 73, Cr — 25, Mo — 1, W — 0.7, Mn — 650, Co — 10, Ni — 17, Cu — 20, Zn — 45, Cd — 2.3(?), Hg — 0.03, Sn — 3, Pb — 21 и As — 2.2. Вычисленные фоновые содержания перечисленных элементов (C_{BG}) вполне сопоставимы с их средними содержаниями в верхней континентальной коре (C_{UC} — Wedepohl, 1995). Вычислены следующие значения коэффициентов концентрации (C_{BG}/C_{UC}): Cu 1.40 — V 1.38 — Sc 1.29 — Pb 1.24 — Mn 1.23 — Sn 1.20 — As 1.10 — Ti 0.95 — Ni 0.91 — Sr 0.89 — Zn 0.87 — Co 0.86 — Ba 0.76 — Mo 0.71 — Cr 0.71 — Be 0.65 — Hg 0.54 — W 0.50. За исключением Cd, фоновые содержания всех исследованных элементов (Be, Sr, Ba, Sc, Ti, V, Cr, Mo, W, Mn, Co, Ni, Cu, Zn, Hg, Sn, Pb и As) в горных породах Болгарии являются не только вполне надежными геохимическими стандартами, подходящими для геохимических, петрологических, металлогенических и экологических исследований, но и региональными кларками для территории Болгарии и Балканского региона.

Abstract: Reference values for the mean background (normal) contents and the upper background thresholds in the main types of rocks and total for all rocks in Bulgaria are derived for chemical elements known as minor and trace components in the composition of the rocks — Be, Sr, Ba, Sc, Ti, V, Cr, Mo, W, Mn, Co, Ni, Cu, Zn, Cd, Hg, Sn, Pb and As. The concentration and the distribution of the elements studied in rocks on Bulgarian territory are characterized through generalization and mathematical-statistical processing of the available data from geochemical investigations carried out during the period 1960–2003. The massif of data assembled includes 19443 quantitative and semi-quantitative element determinations on 2589 samples representative for different by age and geological position rock complexes. The individual types of rocks are characterized by specific parameters of distribution of the elements contents — mean value, variance, upper background threshold, etc. Some of the elements show significant geochemical differentiation between rock types. The ultrabasic and basic rocks are distinguished with high contents of Ti, V, Cr, Ni, Co, Mn. Regarding Be and Pb, highest concentrations are found in the

acid and moderate acid rocks. Most intensively differentiated by rock types are the contents of Ti, Cr, Ni, Hg. The mean contents derived for all rocks on Bulgarian territory are the following (in ppm): Be — 2, Sr — 280, Ba — 506, Sc — 9, Ti — 2956, V — 73, Cr — 25, Mo — 1, W — 0.7, Mn — 650, Co — 10, Ni — 17, Cu — 20, Zn — 45, Cd — 2.3(?), Hg — 0.03, Sn — 3, Pb — 21 and As — 2.2. The background contents obtained for the elements studied (C_{BG}) show good coincidence with the respective recent averages for the upper continental crust (C_{UC}) calculated by Wedepohl (1995). The coefficients of concentration (C_{BG}/C_{UC}) are: Cu 1.40 — V 1.38 — Sc 1.29 — Pb 1.24 — Mn 1.23 — Sn 1.20 — As 1.10 — Ti 0.95 — Ni 0.91 — Sr 0.89 — Zn 0.87 — Co 0.86 — Ba 0.76 — Mo 0.71 — Cr 0.71 — Be 0.65 — Hg 0.54 — W 0.50. The reference values obtained for the background contents of Be, Sr, Ba, Sc, Ti, V, Cr, Mo, W, Mn, Co, Ni, Cu, Zn, Hg, Sn, Pb and As (Cd excluded) could be accepted as sufficiently reliable standards for comparative geochemical, petrological, metallogenic and ecologic investigations and as regional Clarkes of these elements for the Bulgarian territory and the Balkan region.

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Key words: minor and trace elements in rocks, background contents, regional Clarkes.

Introduction

Understanding of the background element contents is based on Vernadskiy's law: the chemical elements are spread and dispersed comparatively uniformly and ubiquitously in the Earth crust; the dispersed spreading is a normal and common state of existence of the elements (Вернадский, 1954). All types of natural formations (rocks, soils, water, air, plants, etc.) are characterized by their own comparatively stable element content's levels which are considered as background ones.

The background contents of the chemical elements in the rocks may be assessed as the following reference values: (a) global values, also known as "Clarkes" (Darnley, 1995; Овчинников, 1990) — determined for the Earth crust and/or its layers; (b) regional values (regional Clarkes) — obtained for considerably large territories; (c) local geochemical background — characteristic for limited, restricted areas, landscapes, etc. Reference values for background concentrations of the elements can be obtained by generalizing in a given hierarchical level, elaborating and interpreting the available analytical data on the element contents.

On the theoretical basis cited above one of the most significant results of the geochemical investigations carried out during the 20-th century is the derivation of geochemical standards — reference values for the mean element contents (Clarkes) in the main types of rocks and in general for the Earth crust, only for the continental crust, for its upper and lower layers, etc. — Turekian & Wedepohl (1961), Виноградов (1962), Овчинников (1990), Ярошевский (1990), Wedepohl (1995), Rudnick & Gao (2003) and others. These studies concern mainly the upper continental crust which represents 31.7% of the Earth crust exposed on the surface and accessible for investigations. At the same time similar assessments have been obtained also for some individual regions and countries, for example, for Australia, Canada, Finland, Germany, Great Britain, In-

dia, Portugal, Russia, USA, etc. (cited in Wedepohl, 1995 and Rudnick & Gao, 2003), for China (Gao et al., 1998; Tong, 1995), Central Kazakhstan (Глухан, Серых, 2000) and others.

The geochemical problem for the element background concentrations in the rocks was elaborated in Bulgaria in the 60-ies of the past century when the first quantitative assessments of concentrations of some minor and trace elements in rocks have been published by E. Alexiev. During the last 40 years, in connection with different geochemical, petrological, lithological, metallogenic and environmental investigations, a significant information on the concentrations of a great number of chemical elements in individual kinds of rocks in different regions of the country has been piled up. With a broader scope are the investigations on the geochemistry of the granitoids in Bulgaria (Alexiev et al., 1980 — unpublished), on the crystalline basement of South Bulgaria (Arnaudov et al., 1995 — unpublished) and on the sedimentary rocks of Paleozoic age by S. Yanev. In spite of this, published data for the mean contents of the most of chemical elements in the rocks in Bulgaria are relatively rare.

Systematic investigations of the data for the contents of minor and trace elements in the rocks on the Bulgarian territory are carried out and published from the authors in the period 2000–2005: for heavy metals and arsenic — Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Hg and Pb (Kuikin et al., 2001) and for lithophile elements — Be, Sr, Ba, Sc, Ti, V, Mo, W and Sn (Christova & Christov, 2005).

The present geochemical study is pointed on the contents in the rocks in Bulgaria of nineteen elements known as minor and trace components in the chemical composition of the rocks — Be, Sr, Ba, Sc, Ti, V, Cr, Mo, W, Mn, Co, Ni, Cu, Zn, Cd, Hg, Sn, Pb and As. The aims of the investigation are: 1) to generalize the earlier studies of the authors on the same problem; 2) to improve and confirm on a broader basis the results obtained for background contents of these elements in the main types of rocks

and for all rocks on Bulgarian territory; 3) to outline the specific features of the distribution in the rocks of the elements studied.

The background values here established could be very useful and necessary as a basis for comparative geochemical, petrological and metallogenic investigations and assessments of rock alterations, ore deposits and anomalies, environmental pollution, in the landscape geochemistry, etc.

Materials and methods

The assessment of the background contents of the elements studied is completed through assembling, processing and generalizing of the available geochemical data from the investigations published in Bulgaria during 1960–2003 period. The list of 96 publications used as sources of data for concentrations of the elements studied in the rocks is given in Appendix 1. Data are obtained also from 26 unpublished sources — reports, kept in the National Geofund¹.

The total number of the rock samples assembled is 2589. Not all of the elements have been determined through individual investigations, because of that the number of analyses for each element is different. The total number of the element determinations used in the created massif of data is 19 443. The data for As, Cd and Hg, partially — for W, are quite limited, but are also quoted here as far as they reflect the state of the investigations up to year 2003.

The available samples from outcrops, sometimes — from boreholes, cover irregularly the country, mainly its mountainous regions, where the rocks occur on the surface. More-or-less dense the samples represent the following rock complexes: Pliocene sedimentary rocks from Sofia basin; terrigenous, clayey and carbonate rocks of Paleozoic and Mesozoic age from Central Balkan Mountains and Strandzha Mountains; intrusive, subvolcanic and volcanic rocks from Western and Central Balkan, Western and Central Sredna Gora zone, Mountains of Rila, Pirin, Rhodopes, Strandzha, Sakar, South Bulgarian granitoids; metamorphic rocks from Balkan, Rila, Pirin, Vlahina and Rhodopes Mountains; ophiolitic complexes from Western Balkan.

Magmatic, metamorphic and sedimentary rocks without described hydrothermal alterations only are included in the massif of data. In the total number of samples (2589) magmatic rocks are 1591 or 61%, metamorphic rocks — 739 or 29% and sedimentary rocks — 259 or 10%. This proportion is close to the

standard profile of the upper continental crust used by Wedepohl (1995) for calculating the average element contents — respectively 56% magmatic rocks (granites, granodiorites, tonalites, gabbros), 30% metamorphic rocks (gneisses, amphibolites, mica schists, marbles) and 14% sedimentary rocks (shales, siltstones, sandstones, limestones).

On a second hierarchical level the samples assembled, according to the petrographic descriptions in the sources used, are systematized into 15 groups giving the possibility of comparing the generalized data for Bulgaria with the adopted in the international practice reference values for mean contents of the elements for the main types of rocks.

Each group contains rock varieties as following: 1) Clastic rocks — gravelites, sandstones, siltstones, etc.; 2) Clay rocks — argillites, shales, etc.; 3) Carbonate rocks — limestones, marls, etc.; 4) Terrigenous-carbonate rocks — flysh and flyshoid rocks; 5) Ultrabasic magmatic rocks — picrites, dunites, peridotites, etc.; 6) Basic magmatic rocks — basalts, diabases, gabbros, etc.; 7) Intermediate magmatic rocks — andesites, diorites, trachyandesites, monzonites, syenites, etc.; 8) Moderate acid magmatic rocks — dacites, granodiorites, etc.; 9) Acid magmatic rocks — rhyolites, granites, etc.; 10) Ultrabasic metamorphic rocks — serpentinites, metaophiolites, etc.; 11) Basic metamorphic rocks — orthoamphibolites, metabasites, etc; 12) Intermediate metamorphic rocks — metadiorites, spilites, quartz amphibolites, etc.; 13) Acid metamorphic rocks — gneisses, gneiss-schists, migmatites, etc.; 14) Carbonate metamorphic rocks — marbles; 15) Low-grade metamorphic rocks — green schists, phylites, metapelites, etc.

The analytical determination of the concentrations of the elements studied in the rocks has been made by different analytical methods. Initially “wet” chemical methods and quantitative and semi-quantitative atomic-emission spectral analysis (AES) were used. The old AES data from the 60-ies years (when only the interval of concentrations has been measured) for this study have been rejected. During the last decades more widely have been applied the methods of X-ray fluorescence analysis (XRF), neutron-activation analysis (NAA), atomic-absorption spectrometry (AAS), atomic-emission spectral analysis with inductively coupled plasma (ICP-AES). In some cases a modern analysis through inductively coupled plasma mass-spectrometry (ICP-MS) was applied. The uncertainty of the above-mentioned quantitative analytical methods varies mainly from 5–10% to 15–20%, and in some earlier studies with AES — up to 30%.

From the database with the contents of Be, Sr, Ba, Sc, Ti, V, Cr, Mo, W, Mn, Co, Ni, Cu, Zn, Cd, Hg, Sn, Pb and As in the rocks of Bulgaria, 15 populations of data for the main rock types are formed, and one total population for all the rocks, as well. On thus formed populations of data a standard mathematical-statistical processing is made.

Many factors determine *a priori* non-homogeneity of the data: 1) the incorporation in a given group of a considerable number of rock varieties of differ-

¹ Алексиев Е. и др. (1980); Арнаудов В. и др. (1995); Байрактаров И. и др. (1996); Велев В. и др. (1999); Игнатовски П., И. Байрактаров (1990); Казълова-Станкова Т. (1994); Каменов Б., Б. Маврудчиев, Р. Неделков и др. (1993; 1994, 1994); Ковачев В. (1975); Куйкин С. и др. (1969; 1973; 1975; 1979; 1981; 1993; 1994; 1995); Панайотов А. и др. (1980); Саров С. и др. (1994; 1995; 1996; 1997; 1998; 1999); Тарасова Е. и др. (1992).

ent geological structures and ages, 2) the long period of the investigations carried out (40 years), 3) the great variety of methods for collecting and for analysis of the samples in different laboratories, and 4) the generally greater variability of trace elements in the rocks. These factors cause the accumulation of different natural and technical dispersions in the statistical populations which reflect in the distribution law.

The statistical criteria for normality of the distribution of element contents by kurtosis and skewness show that the cases of normal or lognormal distributions are comparatively rare. The cumulative curves of content distribution for the most of the elements studied are asymmetric. Such cases are frequent in the geochemical practice and need the use of robust statistical estimates of the mean (average) contents. For this reason the mean element contents are often preferably estimated by the median (Darnley, 1995) which is a non-parametric estimate, without influence from the distribution law.

In the present investigation a mathematical apparatus is used (Юфа, Гурвич, 1964), by which for the mean (expected) value is accepted the median (Md). The variance is evaluated through the quartiles (Q_1 and Q_3) and the relative quartile deviation — D_q (Станев и др., 1971), the last used also for assessment of the degree of geochemical differentiation of the elements in all rocks (Куйкин и др., 1979).

The upper background threshold of the concentrations (UBT), with a given significance level q , was calculated by the formula (Юфа, Гурвич, 1964):

$$UBT_q = Md + 0.5\sqrt{3/q}(Q_3 - Md). \quad (1)$$

$q = 0.05$ was accepted (respectively probability $P = 95\%$), which is the most frequent practice with the mathematical-statistical evaluations.

Some authors propose the determination of UBT to be done through taking into account the respective percentiles (p) along the cumulative curve of distribution of the concentrations, for example, 98 p , 95 p (Van de Meent et al., 1990). In most of the cases here UBT is calculated by the formula (1) and when the number of the respective element determinations is small ($15 \geq N \geq 8$) UBT is provisionally accepted as equal to 95 p .

The purpose of the method of Yufa and Gurvich is through the quartiles to avoid the effect of the so-called “heavy” (hanging) tails of the right side of the cumulative curves under the influence of extremely high values. In the parent populations such extremely high concentrations were found for the most of the elements studied here, for example (in ppm): Be — 68, Ba — 11870, Cr — 4890, W — 300, Mn — 15500, Co — 708, Cu — 2000, Zn — 1000, As — 300, Hg — 50, Pb — 1360. These values may be assessed as obviously anomalous ones. For data filtration (elimination of such “hurricane” element contents) the same expression (1) is used with $q = 0.01$.

Results and discussion

Among the characteristics derived for the elements concentrations the most important are the mean background content (C_{BG}), equal to the median (respectively 50 p), and the upper background threshold (UBT). The concentrations surpassing UBT for a given type of rocks may be treated as anomalous.

Reference values are obtained for the background contents of 18 elements — Be, Sr, Ba, Sc, Ti, V, Cr, Mo, W, Mn, Co, Ni, Cu, Zn, Hg, Sn, Pb and As in 15 types of rocks (Table 1) and total for all the rocks in Bulgaria (Table 2). The valuations for Cd are dubious and the element is excluded from the discussion and the conclusions because of need of new analytical data.

Background values for rock groups. The determined mean contents of the elements into the rock types/groups are different. They often show significant geochemical differentiation. Two opposite patterns of change of the element concentrations by rock types are established which are influenced mainly by the geochemical properties of the elements. The elements of iron group — Ti, V, Cr, Ni, Co, Mn — have higher contents in the ultrabasic and basic magmatic and metamorphic rocks while the chalcophile elements Cu and Zn are concentrated in the ultrabasic, basic and intermediate rocks. All above mentioned elements have lower contents in the acid and moderate acid rocks. The lithophile element Be and the lithophile-chalcophile element Pb, reversely, are with highest contents in the acid and moderate acid rocks and lowest in the ultrabasic and basic rocks.

The derived mean element contents in the rock types in Bulgaria in most of the cases are closest to the respective rock Clarkes after Turekian & Wedepohl (1961), considering some modifications in Овчинников (1990). In a small extent they resemble to the data for rock types of Виноградов (1962) — for intermediate rocks and of Ярошевский (1990) — for basic rocks.

Background values for all rocks. The mean element contents derived for all rocks on Bulgarian territory (C_{BG}) are the following (in ppm): Be — 2, Sr — 280, Ba — 506, Sc — 9, Ti — 2956, V — 73, Cr — 25, Mo — 1, W — 0.7, Mn — 650, Co — 10, Ni — 17, Cu — 20, Zn — 45, Cd — 2.3(?), Hg — 0.03, Sn — 3, Pb — 21 and As — 2.2. The contents of Ti and Mn are commonly expressed in their oxide forms, then here obtained mean values are: for $TiO_2 = 0.49\%$ (4939 ppm), for $MnO = 0.08\%$ (839 ppm).

The mean values obtained are compared with the already calculated by other investigators abundance of the elements studied in the Earth crust (Table 3). For most of the elements the values vary in similar range and significant differences are not found, with exception of already mentioned raised cadmium values.

Table 1
Mean contents and upper background concentrations (in ppm) of Be, Sr, Ba, Sc, Ti, V, Cr, Mo, W, Mn, Co, Ni, Cu, Zn, Cd, Hg, Sn, Pb, As in the rocks in Bulgaria

Rock groups	Be ^a	Sr	Ba	Sc	Ti	V	Cr	Mo	W	Mn	Co	Ni	Cu	Zn	Cd	Hg	Sn	Pb	As
1. Clastic rocks (102 samples)	2.5	167	430	12.9	3600	84.7	30	1.7		467	10	22	28.5	60		0.02	2.4	24	5.6
	5	604	843	18.6	9405	235	119	4.6	n.d. ^b	1630	17.2	53	96.2	137	n.d.		4.6	47.2	
	13	76	79	15	49	74	62	29		50	75	64	54	57		3	18	58	4
2. Clay rocks (27 samples)	7	82	568	n.d.	4636	179	61.5	32.5	19	828	18	30	54	66.9	n.d.	n.d.	6	25	6.6
		344	1103		6780	329	148			2000	60	121	100	120			6	14	
	4	13	13		10	26	26	6	4	12	11	26	14	14			6	14	1
3. Carbonate rocks (110 samples)	2	309	80	4	981	20	10	0.7		232	5	29	18	40	n.d.	0.028	1.1	25	14.8
	3	1197	433	14	7235	58.7	22	1.6	n.d.	832	16	52	88	139					
	8	102	104	21	33	81	67	2.3		77	33	21	70	87		2	6	66	2
4. Terrigenous- carbonate rocks (20 samples)	2.2	212	336	11.6	3749	71.2	37.6	1.3		894	11	34.2	32.6	59.4	n.d.	n.d.	1.9	19.5	n.d.
		563	1610	14.2			72.3	1.8		2160	21.5	46	58	78				21.4	
	5	15	20	11	2	7	19	10	n.d.	18	20	8	8	12			5	19	
5. Ultrabasic magmatic rocks (71 samples)	0.3	503	352	n.d.	838	84.1	1620	0.3		876	55.1	1410	118	85	n.d.	n.d.	n.d.	10	3.2
		853	2860		4844	477	4070	2		2610	268	3610	788	145				33	
	7	10	17		14	34	43	14		44	41	43	16	16				15	1
6. Basic magmatic rocks (123 samples)	0.6	522	655	20.6	5923	181	90.2	1.6	19	1240	28	39	43	74.5	2	0.07	2	10	2
	2.8	1211	1990	38.9	7426	372	696	7		2140	51	192	151	124			5.9	49	
	9	75	79	36	19	70	94	27	6	94	77	80	77	76	5	1	16	73	3
7. Intermediate magmatic rocks (367 samples)	1.5	575	609	14.8	3098	140	21.9	1.2	10	975	14	20	40	61	2.7	0.003	3	21.5	2.86
	3.5	1335	2123	26	4128	374	131	8.2	25.5	1700	39	58.7	115	154	7.7	0.47	10.7	93.2	8.51
	44	248	288	91	8	172	270	116	11	277	250	218	235	262	32	8	78	219	36
8. Moderate acid magmatic rocks (258 samples)	2.6	380	620	4.5	2752	60.5	21.5	1.5	0.5	600	6	14	14	44	2.6	0.20	3	27	1.8
	4.2	1231	2079	25.5	4278	176	132	11.2	4.4	1130	21.5	79.8	72.1	91.4	5.2		14.6	50.2	5.96
	45	192	198	59	15	104	196	97	33	210	185	121	123	176	9	4	60	113	30
9. Acid magmatic rocks (772 samples)	3	280	631	2.6	2034	20.5	8	0.6	0.6	370	3	6	8	28	2	0.06	4	30	1.9
	6.9	716	1672	7.5	3886	112	54.4	2.2	2.1	1140	14.6	35	39	83.1		0.36	11.7	68.7	6.93
	178	517	576	125	19	304	490	287	127	484	484	347	382	464	7	10	306	532	55

Table 1
(continued)

Rock groups	Be ^c	Sr	Ba	Sc	Ti	V	Cr	Mo	W	Mn	Co	Ni	Cu	Zn	Cd	Hg	Sn	Pb	As				
10. Ultrabasic metamorphites (28 samples)	1	25	65	7.4	778	50	202	3	n.d. ^b	1050	99	428	20	96	n.d.	n.d.	3	5	n.d.				
		480	617		1101	375	7510			2100	125	2400	66	270							2	5	
	2	14	16	1	14	13	17	2		16	16	15	9	10							2	5	
11. Basic metamorphites (271 samples)	0.8	195	122	30	8152	203	106	1	n.d.	1240	34	50	28.5	61	n.d.	n.d.	2	5	0.5				
	1.6	563	707	45.5	18845	538	717	4.9		2440	66.9	189	115	212						11.3	16.6		
	24	257	224	45	65	222	249	25		230	231	221	150	119						29	105	1	
12. Intermediate metamorphites (57 samples)	1	248	454	13.9	6402	156	34.4	1.5	n.d.	852	13.4	20	20.7	54.8	n.d.	n.d.	1	15.5	n.d.				
		777	853	51	10461	237	195	3.4		2130	43.9	39	60.5	217						6	24		
	6	54	57	18	12	33	46	11		36	34	18	16	31						3	20	2.8	
13. Acid metamorphites (312 samples)	3	189	655	11.1	419	50	33.6	1	30	387	11	10	20	50	2.4	n.d.	3	20	2.8				
	5	619	1555	21.5	1576	244	235	7.3	48	1440	30.9	95.1	74.2	185	3			8.8		58.7			
	23	281	298	66	21	213	277	55	9	219	207	137	125	187	8			38		193	4		
14. Carbonate metamorphites (26 samples)	0.5	126	207	0.7		23	4.3	0.2	n.d.	232	2.8	5.0	14	17	n.d.	n.d.	1	11.5	0.5				
		412	567		n.d.	129	77.6	1.7		700	22.1	37.9	60.4	92						4	22		
	5	23	19	4		19	22	8		13	24	19	21	15							4	22	1
15. Low-grade metam. rocks (45 samples)	2.2	85	641			55	35	1.9	n.d.	610	10	30	9.5	30	10	n.d.	2.7	7.5	0.5				
		409	1527	n.d.	n.d.	229	93.1	6.3		2774	43.3	102	57.9	222						6	36		
	6	28	39			30	38	9		36	39	41	38	40	2					6	36	1	
All rock types combined (2589 samples)	2	280	506	9.4	2956	72.9	24.8	1	0.7	650	10	17	20	45	2.3	n.d.	3	21	2.2				
	5.9	1015	1675	34.8	13320	378	204	4.9	3.5	2270	48.7	106	105	153	5.8			14.6		63.6	7.4		
	379	1905	2027	492	281	1402	1916	719	190	1816	1727	1379	1338	1566	63			580		1494	139		

^a For each element: row I (bold) — mean value (median); row II — upper background threshold determined by formula (1) at $N > 15$ or by 95 percentile at $15 \geq N \geq 8$; row III — number of samples analyzed for the element (N); ^b No data for the element

Table 2
Statistical characteristics of the contents of the elements studied in all rocks on Bulgarian territory

Characteristics	Be	Sr	Ba	Sc	Ti	V	Cr	Mo	W	Mn	Co	Ni	Cu	Zn	Cd	Hg	Sn	Pb	As
Element determinations number (N)	379	1905	2027	492	281	1402	1916	719	190	1816	1727	1379	1338	1566	63	30	580	1494	139
Minimum content, ppm	0.3	3	0.5	0.01	20	0.5	0.18	0.01	0.1	5	0.03	0.2	0.002	1	0.1	0.0002	0.15	0.46	0.15
Maximum content, ppm	10	6500	5000	85.6	21594	650	4516	300	50	3330	197	2852	804	300	10	0.5	30	246	36
Average (\bar{x}), ppm	2.52	347	612	11.3	3807	109	108	2.76	3.59	743	15.7	77.3	32.0	53.1	2.76	0.12	4.23	25.8	3.49
Standard error of the average ($S_{\bar{x}}$), ppm	0.10	6.89	12.1	0.46	215	2.95	7.63	0.46	0.61	12.4	0.48	8.05	1.23	1.06	0.30	0.03	0.16	0.58	0.42
Confidence level ($\beta_{0.05}$), ppm	0.19	13.5	23.8	0.91	424	5.79	15.0	0.91	1.20	24.2	0.94	15.8	2.42	2.09	0.60	0.06	0.32	1.15	0.84
Standard deviation (σ), ppm	1.85	301	547	10.2	3612	110	334	12.5	8.37	526	20.0	299	45.1	42.1	2.39	0.17	3.92	22.6	4.99
Coefficient of variation (V), %	73.6	86.7	89.4	90.3	94.9	102	310	451	233	70.8	127	387	141	79.3	86.5	142	92.5	87.6	143
Kurtosis (E)	3.60	93.9	8.64	6.98	1.68	3.32	50.5	459	11.8	1.54	19.9	41.7	103	5.48	2.28	0.26	7.88	19.0	18.8
Skewness (A)	1.60	5.61	2.25	1.92	1.28	1.73	6.50	19.9	3.39	1.06	3.59	6.42	7.6	1.77	1.41	1.34	2.35	3.04	4.01
Percentile 25 (I quartile Q_1), ppm	1	157	230	3.6	838	27	8	0.5	0.41	310	4	6	8	24	1.6	0.005	1.45	10	1.2
Median (Md, 50p), ppm	2	280	506	9.36	2956	72.9	24.8	1	0.7	650	10	17	20	45	2.3	0.03	3	21	2.2
Percentile 75 (III quartile Q_3), ppm	3	470	808	15.9	5634	152	71	2	1.43	1070	20	40	42	73	3.2	0.168	6	32	3.55
Relative quartile deviation ($D_{0.75}$), %	50.0	49.9	55.7	63.1	74.1	69.8	79.7	60.0	55.4	55.0	66.7	73.9	68.0	50.5	32.8	94.2	61.1	52.4	49.5
Upper background threshold ($UBT_{0.05}$), ppm	5.87	1015	1675	34.8	13320	378	204	4.87	3.53	2270	48.7	106	105	153	5.78	0.56	14.6	63.6	7.42

Table 3

Comparison between background contents obtained for Bulgaria and actual Clarke values of Be, Sr, Ba, Sc, Ti, V, Cr, Mo, W, Mn, Co, Ni, Cu, Zn, Cd, Hg, Sn, Pb, As (in ppm)

Element	Clarke after Vinogradov (1962)	Clarke after Ovchinnikov (1990)	Average for UC after Wedepohl (1995) – C _{UC}	Value for UC after Rudnick & Gao (2003) – C _{R&G}	This study background content – C _{BG}
Be	3.8	2	3.1	2.1	2
Sr	340	370	316	320	280
Ba	650	470	668	628	506
Sc	10	17	7	14.0	9
Ti	4500	5300	3117	3830 *	2956
V	90	12	53	97	73
Cr	83	93	35	92	25
Mo	1.1	1.2	1.4	1.1	1
W	1.3	1.4	1.4	1.9	0.7
Mn	1000	900	527	775 *	650
Co	18	23	11.6	17.3	10
Ni	58	70	18.6	47	17
Cu	47	53	14.3	28	20
Zn	83	68	52	67	45
Cd	0.13	0.17	0.102	0.09	(2.3)
Hg	0.083	0.072	0.056	0.05	0.03
Sn	2.5	2.3	2.5	2.1	3
Pb	16	13	17	17	21
As	1.7	1.8	2.0	4.8	2.2

* calculated from the oxide form content

More detailed comparison is made with the average data recently calculated from earlier results for composition of the upper continental crust by Wedepohl (1995) – C_{UC} and Rudnick & Gao (2003) – C_{R&G}.

According to the values of the coefficients of concentration $C_c = C_{BG}/C_{UC}$ the elements studied form the following row:

Cu 1.40 – V 1.38 // Sc 1.29 – Pb 1.24 – Mn 1.23 – Sn 1.20 – As 1.10 – Ti 0.95 – Ni 0.91 – Sr 0.89 – Zn 0.87 – Co 0.86 – Ba 0.76 – Mo 0.71 – Cr 0.71 // Be 0.65 – Hg 0.54 – W 0.50.

The values for Sc, Pb, Mn, Sn, As, Ti, Ni, Sr, Zn, Co, Ba, Mo and Cr are nearly equal to their averages for upper crust after Wedepohl (1995) – $C_c = 1 \pm 0.3$. The range ± 0.3 corresponds to the uncertainty of the chemical methods of elements determination which reaches 30 %. For many trace elements Rudnick & Gao (2003) accept similar uncertainty within 30 %.

The values obtained for 5 elements differ more significantly: Cu and V are increased ($C_c > 1.3$) while the mean contents of Be, Hg and W are found decreased (40 % and more below the averages after Wedepohl, 1995).

The comparison with the most actual mean values recommended by Rudnick & Gao (2003) shows that the total mean values here obtained are almost systematically decreased. The coefficients of concentration $C_c = C_{BG}/C_{R\&G}$ form the following row:

Sn 1.43 // Pb 1.24 – Be 0.95 – Mo 0.91 – Sr 0.88 – Mn 0.84 – Ba 0.81 – Ti 0.77 – V 0.75 – Cu 0.71 // Zn 0.67 – Sc 0.64 – Hg 0.60 – Co 0.58 – As 0.46 – W 0.37 – Ni 0.36 – Cr 0.27.

The range of $C_c = 1 \pm 0.3$ includes the background values obtained for Pb, Be, Mo, Sr, Mn, Ba, Ti, V and Cu while different are the values for 9 elements: Sn is increased and Zn, Sc, Hg, Co, As, W, Ni, Cr are decreased in comparison with the results of Rudnick & Gao (2003).

Published data for element contents in the lower continental crust and for the bulk crust composition (Wedepohl, 1995; Rudnick & Gao, 2003) differ more significantly from the obtained for Bulgarian rocks main values which are nearest to the data for upper continental crust.

The estimates for trace elements contents in the rocks show more variation from study to study (Rudnick & Gao, 2003). In spite of this the most of total background values here established agree within 30 % the recent estimates of the composition of the upper continental crust. The values obtained for Bulgarian territory are closest to the respective element averages calculated for the upper crust by Wedepohl (1995) – Figure 1.

Another aspect of the distribution of the elements studied in the rocks is their different degree of geochemical differentiation in the total population. According to the increasing values of the relative quartile deviation (D_Q), this differentiation is expressed in the following rank:

Be 50 – Sr 50 – As 50 – Zn 51 – Pb 52 – W 55 – Mn 55 – Ba 56 – Mo 60 – Sn 61 – Sc 63 – Co 67 – Cu 68 – V 70 – Ni 74 – Ti 74 – Cr 80 – Hg 94.

Most intensively differentiated between rock types are the contents of the elements Hg, Cr, Ti, Ni, V, Cu and Co.

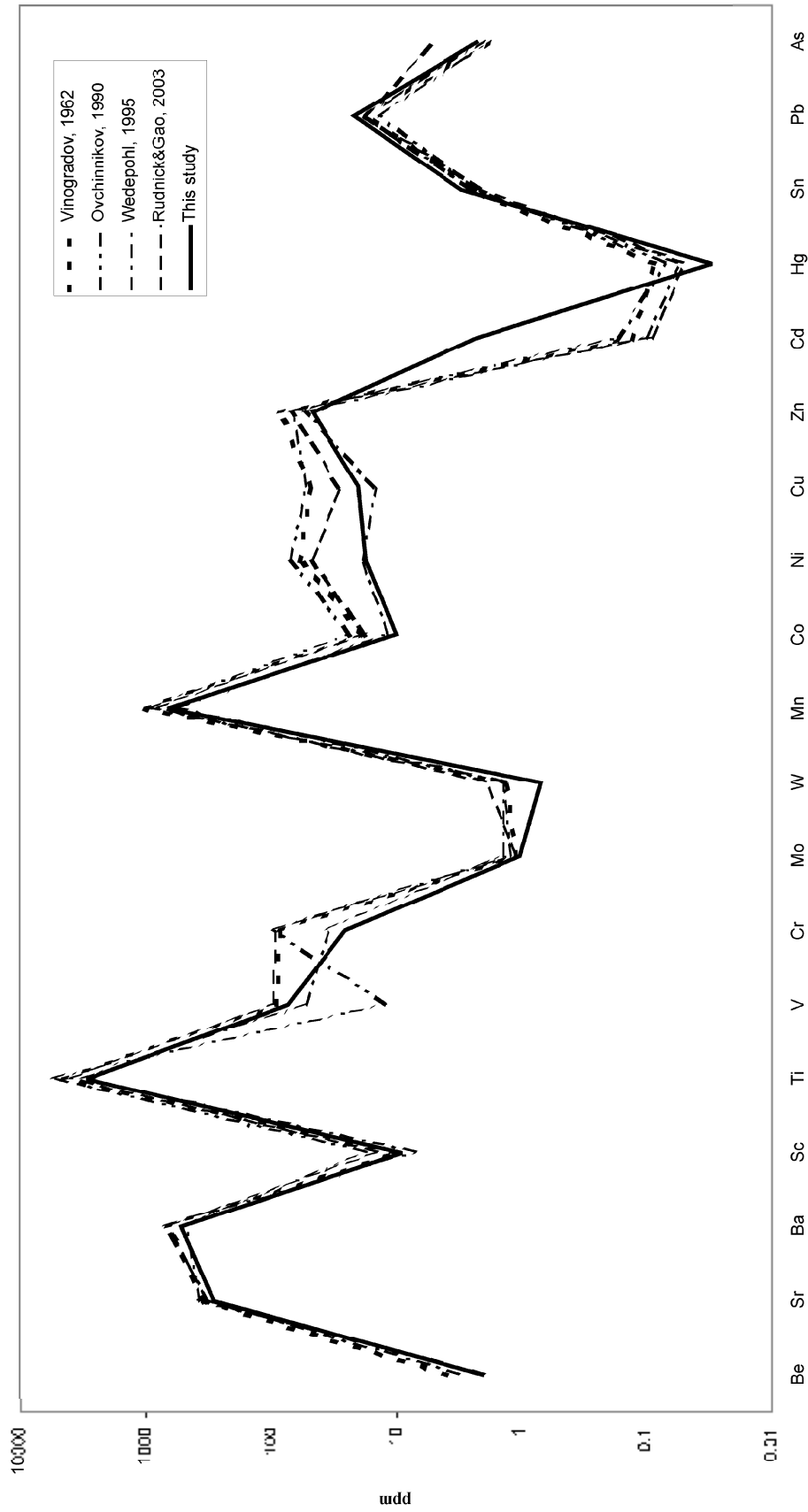


Fig. 1. Mean values of Be, Sr, Ba, Sc, Ti, V, Cr, Mo, W, Mn, Co, Ni, Cu, Zn, Cd, Hg, Sn, Pb and As for Upper continental crust compared with the background values obtained for Bulgarian territory

Upper background thresholds. The values calculated for the upper background threshold ($UBT_{0.05}$) of the element contents (Tables 1 and 2) give a general idea of the upper limit of normal element concentrations in the rocks most widely spread in Bulgaria. Each rock group has its specific UBT for the individual elements, which may be lower or higher than the respective total UBT for all the rocks (Table 1).

The upper background threshold marks the limits of the normal concentrations. This value is first of all applicable for the rock groups, while for the total population of all rocks UBT has an approximate character because of the element differentiation between rocks with different chemical and mineral composition and different genesis. The total upper background threshold for all types of rocks combined, applied to some rock types, would exclude a part of the background samples as anomalous, and for other types it would include anomalous samples into the category of the background ones. For example, the total UBT for Ni is 106 ppm, but the UBT in the ultrabasic and basic rocks where the same element is concentrated are respectively 3610 ppm and 192 ppm (Table 1).

The width of the interval between upper background threshold and mean content (C_{BG}) is different for the individual elements. It depends on the variance of the background contents. According to the values of the ratio $UBT_{0.05}/C_{BG}$ (Table 2) the elements considered form the following order: Be 2.9 — Pb 3.0 — Ba 3.3 — Zn 3.4 — As 3.4 — Mn 3.5 — Sr 3.6 — Sc 3.7 — Ti 4.5 — Co 4.9 — Mo 4.9 — Sn 4.9 — W 5.0 — V 5.2 — Cu 5.3 — Ni 6.2 — Cr 8.2 — Hg 18.7.

Excluding the endmost member of the row (Hg) the ratio $UBT_{0.05}/C_{BG}$ varies from 3 to 8, at an average about 4.

On lower hierarchical levels (for example, for landscapes, geological-structural or administrative regions, different rock complexes, etc.) the parameters of the background concentrations (mean content and upper background threshold) of the elements may have their specific local values, includ-

ed statistically in the general estimates obtained for the whole Bulgarian territory.

Conclusion

The reference values derived for the mean background contents of Be, Sr, Ba, Sc, Ti, V, Cr, Mo, W, Mn, Co, Ni, Cu, Zn, Hg, Sn, Pb and As may be accepted as sufficiently reliable geochemical standards, characterising the chemical composition of the rocks on Bulgarian territory.

The background values established are based on real results from quantitative chemical analyses published in Bulgarian geochemical studies during a period of 40 years. In spite of the local representativity of the rock samples (for the country) the values derived show good coincidence with the recently calculated averages of the studied elements in the upper continental crust.

The content of Cd in the rocks in Bulgaria needs additional investigations and first of all — new data obtained through highly sensitive modern analytical methods.

The results obtained show that there is no “one single” background value for given element, which can be equally valid for all types of rocks. The individual rock groups are distinguished with specific parameters of distribution of the background concentrations (mean value, variance, upper background threshold, etc.) which often are significantly different from each other, especially for the contents of the most intensively differentiated elements — Hg, Cr, Ti, Ni, V, Cu and Co.

The reference background values obtained for 18 elements known as minor and trace components in the chemical composition of the rocks — Be, Sr, Ba, Sc, Ti, V, Cr, Mo, W, Mn, Co, Ni, Cu, Zn, Hg, Sn, Pb and As — may have a multipurpose application for comparative geochemical, petrological, lithological and metallogenic investigations, for assessment of the quality of the environment (soils, etc.) and as regional Clarkes of these elements for the Bulgarian territory and the Balkan region, as well.

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Appendix 1

Publications — sources of data for the contents of Be, Sr, Ba, Sc, Ti, V, Cr, Mo, W, Mn, Co, Ni, Cu, Zn, Cd, Hg, Sn, Pb and As in the rocks on Bulgarian territory

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