

Geology

The First Data on Industrial Concentration of Thorium and Bismuth in Hydrothermally Altered Lower-Jurassic Clay-Shales of the Stori Canyon (Southern Slope of the Greater Caucasus, Kakheti)

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ABSTRACT. On the southern slope of the Greater Caucasus, the river Stori canyon (Kakheti) exposes fractured, cataclastic and mylonitized Lower Jurassic clay-shales, which at more than 3 km distance undergo intensive hydrothermal silicification, carbonization and sulphide mineralization. This process is particularly intensively revealed in brecciated zones, where sometimes thick sulphide ore lodes are formed. The studies carried out by us showed that this entire complex of rocks in the described hydrothermal alteration process was enriched with thorium and bismuth up to industrial concentration (Th-100-200 g/t; Bi-200-900 g/t). This enrichment was especially intensively revealed in quartz-pyrite-pyrrhotine-copper pyrite veins, where the content of these elements reaches the level of the world class deposits (Th-0.3842%; Bi-0.4806 %; chemical analyses of thorium and bismuth have been performed in Vancouver "ACMELABS" laboratory, Canada, using the ICP-OSL method). The authors consider that this discovery has significant strategic and economic value; hence hydrothermally altered Lower-Jurassic clay-shales of the Stori canyon need further urgent detailed study. © 2011 Bull. Georg. Natl. Acad. Sci.

Key words: thorium, bismuth, clay- shales, the Greater Caucasus, Kakheti.

Thorium represents the 90th element of the periodic system, belongs to actinoides and in natural conditions is represented by solid phase. It has the highest melting (1824°C) and boiling (4788°C) temperature among the known elements on earth. Pure thorium is a silvery-white element, which maintains its colour on the earth surface for several months, but as a result of oxidation it first obtains grayish-yellow colour and then transforms into black loose mass. Thorium is used for manufacturing high-temperature and high-technology devices, but its most significant property is the fact that, like uranium and plu-

tonium, it can be used as fuel in nuclear reactors [1]. However, compared with these elements, thorium has quite a number of priorities: is more widely spread; in comparison with uranium its extraction is rather cheap; is less radioactive; full annihilation of its waste is possible; produces 200 times more energy than uranium; using its waste for the creation of a nuclear bomb is impossible. Due to such unique properties and the present complicated energy situation, it is considered to be the 3rd millennium energy industry of the future. Nowadays the world's developed countries, including India and China, are work-

ing on a project for modernized reactor creation and it is planned that in the nearest 10 years these reactors will fully replace uranium reactors [2].

Bismuth is the 83rd element of the periodic system. It is represented by the solid phase and has grayish-yellow colour, often with rosy tint. In the earth's crust it is not widely spread and is approximately twice more than gold. Its melting temperature is (271.5°C) and that of boiling - (1564°C). In contrast to lead, it is a nontoxic element and due to this it is widely used in medicine and cosmetic industry. Besides the above mentioned, this element is used in electrical engineering, nuclear reactors as uranium fuel additive agent and in advance technology industry. In 2009 in the whole world 7300 tons of bismuth were extracted and at present the market value of its 1 kg amounts to USD 390 on the average.

As a result of geological works carried out in the Lower-Jurassic silicified and sulphidized clay-shales of the Stori canyon (south slope of the Greater Caucasus, Kakheti), thorium and bismuth industrial concentrations have been found by us for the first time in Georgia. The present article refers to this significant issue.

Field works are being carried out within the project (#GNSF/ST09-1071-5-150) of Shota Rustaveli National Science Foundation, but analytical works have been performed in "ACMELABS" Laboratory, Vancouver, Canada, using the ICP-OSL method and by financial support of the Mining Corporation "Golden Fleece".

Thorium and Bismuth in the Earth's Crust

Thorium is mainly connected with oxide magmatic rocks, its standard content in granitoids makes up 5-8 g/t and it is 3-4 times much more spread in the earth's crust than uranium. Its basic mineral is monazite ($\text{Ce,La,Y,Th}(\text{PO}_4)_3$), occurring as an accessory in granites. Besides these minerals thorium creates silicate mineral thorite (ThSiO_4), which as monazite is mainly an accessory mineral of granites. On the surface thorite turns into its watery variety thorigummite [$\text{Th}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$] and forms loose mass.

Thorium accumulations are observed both in endogenous and exogenous conditions. Among endogenous deposits are singled out magmatic, pegmatitic, scarn and hydrothermal ones. All of them are mainly connected with alkaline acidic magmatic rocks. As thorium isomorphically substitutes calcium, its accumulations are often observed in carbonate rocks. Its industrial content in these deposits oscillates within 0.02-0.3 %. Among exogenous deposits monazite-containing coastal sands should be mentioned, the biggest deposits among them are in Brazil and India.

Some developed countries of the world have calculated thorium reserves. According to the data of 2010 of the United States Geological Survey [4], these reserves are distributed in the following way (in tons): USA - 440.000; Australia - 300.000; India - 290.000; Turkey - 380.000; Norway - 132.000; Canada - 100.000; South Africa - 35.000. It should be mentioned that there is no information about these element reserves in China and Russia.

Bismuth, as well as thorium, is genetically connected with acid intrusives and its standard content in these rocks makes up 0.5-1.0 g/t. This element is formed approximately in the 250^o-400^o C temperature range, mainly at post-magmatic, hydrothermal stage [5]. The basic minerals of bismuth are bismutite (Bi_2S_3 -bismuth sulphide), bismite (Bi_2O_3 -bismuth oxide) and carbonized variety of bismuth oxide - bismuthite [$\text{Bi}_2(\text{CO}_3)_2\text{O}_2$]. It is in association with lead, copper, zinc, gold and other metals and as a rule its extraction is carried out together with these metals. Its industrial concentration oscillates within 0.01%-0.2%. According to the United States Geological Survey [4] the world reserve of bismuth makes up 320000 tons and more than half of this (240000 tons) is concentrated on the territory of Canada.

Brief Geological Description of the Region

The river Stori canyon (the left tributary of the river Alazani, Kakheti) orthogonally intersects the southern slope of the Greater Caucasus, which, according to modern tectonic regionalization, belongs to the Greater Caucasus terrain [6]. The region is located in the Kazbegi-Lagodekhi tectonic zone and is mainly formed of thick clay-shales series, in which sandstone interlayers are observed in small quantities. The whole complex of these sediments extends in the NW-SE direction, with north-eastern 50^o-70^o angle of slope. Clay-shales represent the oldest formations of the region, dated as Early-Jurassic by ammonites [7]. In the structure of the region, together with Lower-Jurassic clay-shales effusive and intrusive magmatic products of - base, average and acid composition take a significant place as well [8].

According to modern geophysical data, the sediments of the Greater Caucasus southern slope in Kakheri sector are located on oceanic type thin crust [9] formed as a result of extension and these magmatic products are probably the result of this process.

The described sediment complex of the Stori canyon for approximately 3 km thickness undergoes intensive fracturing, cataclase, mylonitization, hydrothermal silicification, sulphidization and carbonization (Fig. 1). This process has gone so far that very often it is difficult to determine the initial nature of mother rocks, but the intensive,

exposed hydrothermal altered rocks, identified over a large area, must be indicative of a powerful thermal spring lying under them, as evidenced by multiple magmatic intrusive bodies in the Stori canyon. As for intrusive bodies, they are diverse: starting from base and ending with acid ones.

In the Stori canyon chlorite-sericite-albite and quartz-albite-sericite anchimetamorphic rocks are overlain with cataclastic and hydrothermal transformations. Hydrothermal variation is the further process of cataclasis, in which barren and ore stages are identified. At barren stage anchimetamorphic rock silicification, sericitization and chloritization takes place. At the ore stage sulphide mineralization and carbonization takes place and disseminated, veinlet, disseminated-veined and massive copper-polymetallic mineralizations are formed. This process is particularly intensively manifested in the brecciation zone, where thick sulphide ore lodes are sometimes formed (Fig. 2).

Thorium and bismuth ore manifestation in the Stori canyon

To date there has been no evidence of ore mineralizations of thorium in Georgia. Only single chemical analyses of this element are available, not pointing to any significant high contents. According to G. Odikadze [10], in the granites of the Greater Caucasus and Dzirula massif uranium content is lower than normal, but that of thorium is within normal limits. In the basic mass of Dzirula Massif Rkvia granitoid intrusive, uranium content is within 2 g/t, but that of thorium 8 g/t. In the pegmatites of the same intrusive, uranium concentration reaches 8 g/t and thorium 13 g/t [11]. As for bismuth, no data are available in Georgia concerning its distribution.

Last year, within the project of Shota Rustaveli National Science Foundation our team started investigation of prospective gold mineralization at the Greater Caucasus Kakheti segment. By arrangement, we performed analysis in Canada (ACMELABS, Vancouver) of 13 samples from the section of the Stori canyon and of 3 samples from the Alazani river head using the ICP method. The results obtained for the first time in Georgia showed anomalously high industrial contents of thorium and bismuth, respectively - 3842 g/t and 40806 g/t. (Tab. 1 and 2) in one of the quartz-pyrite-pyrrhotine-copper pyrite veins of the Stori canyon (Fig. 2). 13 samples analyzed from the Stori canyon were taken at 3 km distance and comprise almost the entire spectrum of silicified and sulphidized clay-shales. As is seen from these tables, thorium content in these rocks, compared with the standard one (5-8 g/t) is raised almost by one line, oscillating within 50.9 g/t up to 203 g/t. These data are background concentration of these thorium rocks, but taking into account the fact that the



Fig. 1. Cataclastic, silicified and sulphidized Lower-Jurassic clay-shales outcrop in the river Stori canyon.

world class deposits contain this element within 200-250 g/t [4], then it will be clear how much more is thorium potential in the Stori canyon metasomatites, especially as these rocks occur over the surface of more than 3 km.

In altered clay-shales of the Stori canyon larger accumulations of bismuth are observed. As was mentioned above, the standard content of these elements in acidic magmatites varies within 0.5-1 g/t, whereas its background content in these rocks oscillates within the range 200 g/t to 900 g/t, which by itself is very high industrial contents. The much bigger concentrations of thorium and bismuth are recorded in quartz-pyrite-pyrrhotine-copper pyrite vein found by us, formed in the brecciate zone of silicified-sulphidized clay-shales (Fig. 2). It is outcropped over the motorway in 250 m and with 3-10 m thickness runs toward north-west (strike azimuth 20-30, incidence angle 60-70). Due to the complicated relief we were able to trace this vein only along 300 m, though it continues farther. As seen from Table 2. thorium concentration in it makes up



Fig. 2. Quartz-pyrite-pyrrhotine-copper pyrite veins of the Stori canyon with anomalously high content of thorium and bismuth.

3842 g/t (0.3842 %), which is a very high indicator. As mentioned above, in the world class deposits the average content of this element makes up 200-250 g/t [4], though higher concentrations can be observed as well. As for bismuth, this element in this vein is accumulated in much greater concentration, reaching 4806 g/t (0.48 %). As noted above, the largest accumulation of this element in the world is recorded within 0.2 % [3].

On the basis of these data, bismuth content (0.48 %) in the vein found by us proves to be uniquely high. It should be noted that besides thorium and bismuth this vein contains a considerable quantity of copper (11414.62

g/t) and silver (375 g/t), which is a significant factor for its complex treatment. What is more, veins of this type are recorded by dozens in the Stori canyon, though of course not all of them have been found yet.

From the analysis of the above chemical element contents (Tab. 1, 2) it is clear that in the Stori canyon thorium and bismuth is in paragenetic correlation and they were probably deposited by hydro-therms at one and the same time. As for the depth of occurrence of quartz-pyrite-pyrrhotine-copper pyrite veins and their scales, this is a challenge for future investigations. But taking into account the high concentrations of Th, Bi and Ni (73.95 g/t),

Table 1.

The contents of thorium, bismuth and other elements in hydrothermally altered clay-shales of the Stori canyon

Elements	6-08	7-08	8 W -08	8 B -08	9-08	10-08	11-08	12-08
Au(gm/t)	0.02	0.03	<0.01	<0.01	0.04	0.03	0.02	0.01
Mo (PPM)	0.64	0.65	0.67	0.13	0.54	0.94	0.70	0.39
Cu (PPM)	32.78	27.43	26.14	11414.62	66.70	191.31	103.06	64.91
Pb (PPM)	43.14	30.91	5.81	33.32	6.11	18.42	12.68	22.16
Zn (PPM)	10.6	5.8	6.0	0.5	7.3	6.8	7.8	5.9
Ag (ppm)	4.9	7.8	6.1	275.5	17.8	7.2	13.6	12.4
Ni (ppm)	0.03	0.02	0.19	73.95	0.02	0.11	0.56	0.22
Co (PPM)	13.19	4.73	0.40	1.41	0.61	2.11	2.02	6.65
Mn (PPM)	0.55	0.51	0.13	16.48	0.82	0.09	1.03	0.15
Fe (%)	4	2	2	3	32	7	6	11
As (PPM)	0.13	0.19	0.28	20.16	1.23	0.32	0.84	1.09
U (PPM)	0.027	0.012	0.017	0.003	0.071	0.044	0.034	0.055
Au (PPB)	3.5	6.7	4.3	2.1	4.2	5.5	6.3	2.4
Th (PPM)	7.6	11.7	50.9	3842.0	39.0	41.4	203.8	99.0
Sr (PPM)	3600	3770	13	483	787	179	108	84
Cd (PPM)	21.3	6.1	4.2	64.0	40.0	30.7	8.2	37.7
Sb (PPM)	7.1	3.5	3.2	118.3	19.3	13.5	7.9	20.6
Bi (ppm)	57	61	197	4806	881	234	319	396
V (ppm)	5.70	0.99	1.39	18.90<0.1	5.76	2.68	3.00	3.91
Ca (%)	932.2	31.2	2.0	-	6.4	65.7	72.3	87.2
P (%)	1.3	0.7	0.6	0.1	0.6	0.7	0.6	0.6
La (ppm)	17166.2	16628.0	5.9	8.8	3204.9	20.9	12.5	8.1
Sc (ppm)	0.4	0.5	0.4	1.4	2.0	0.6	0.6	1.2
Tl (PPM)	1.23	0.13	0.04	0.04	0.03	0.11	0.06	0.16
S (%)	5.67	0.85	0.28	4.61	1.88	2.18	0.65	2.70
Hg (PPB)	59	20<0.1	5<0.1	119	6	32	22	8
Se (PPM)	0.2			8.8	0.7	0.9	0.6	0.6
Te (PPM)	0.02			1.20	0.11	0.08	0.53	0.03
Ga (PPM)	0.8	0.8	1.4	1.3	5.4	1.0	1.2	1.3
Cr (PPM)	1.8	1.7	1.8	2.6	17.8	12.8	1.5	9.2
Mg (%)	0.09	0.07	0.32	0.18	1.27	0.29	0.24	0.55
Ba (PPM)	17.4	23.3	15.9	9.0	37.8	24.3	31.9	29.6
Ti (%)	0.001	0.002	0.002<1	0.002<1	0.011<1	0.002<1		0.042
B (PPM)	1	2						1
Al (%)	0.30	0.33	0.59	0.33	2.29	0.56	0.44	0.72
Na (%)	0.004	0.006	0.008	0.003	0.023	0.007	0.003	0.006
K (%)	0.18<0.1	0.20<0.1	0.11	0.02<0.1	0.17	0.17	0.10	0.17
W (PPM)	-	-	0.1	-	0.2	0.2	6.3	0.2

Sample #6-08 – weakly silicified clay-shale; #7-08 – phyllitized clay-shale, with single pyrite impregnations; #8W-08 – pyritized quartz-chlorite-sericitic metasomatite; #8B-08 – quartz-pyrite-pyrrhotine-copper pyrite vein; #9-08 – silt slate with quartz-pyritic veinlets; #10-08 – quartz-sericite-pyritic shale; #11-08 and #12-08 – pyrite-quartz-sericite-chloritic shale.

Table 2.

The Contents of thorium, bismuth and other elements in hydrothermally altered clay-shales rocks of the Stori canyon and the river Alazani head

Elements	13-08	14Y -08	14W -08	15-08	16-08	18-09	38-09	41-09
Au (GM/T)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Mo (PPM)	0.59	0.95	0.23	0.70	1.11	0.61	0.21	0.25
Cu (PPM)	20.80	51.49	9.33	38.34	68.10	226.65	24.89	19.22
Pb (PPM)	16.55	11.77	6.09	8.20	6.58	5.24	6.37	4.69
Zn (PPM)	4.8	7.5	9.6	7.1	1.7	5.5	3.5	8.9
Ag (PPB)	4.5	14.0	5.5	29.6	36.7	19.2	15.3	12.4
Ni (PPM)	0.45	0.11	0.01	0.08	0.04	0.06	0.06	0.02
Co (PPM)	2.24	1.52	1.93	1.06	0.65	0.60	1.65	2.43
Mn (PPM)	0.38	0.77	0.03	0.19	0.56	1.73	0.07	0.10
Fe (%)	6	30	17	37	38	21	12	24
As (PPM)	0.23	0.45	0.19	1.23	1.75	2.06	1.20	0.29
U (PPM)	0.033	0.083	0.032	0.048	0.071	0.082	0.017	0.036
Au (PPB)	1.5	15.0	1.8	8.1	6.2	4.3	2.4	2.9
Th (PPM)	127.4	54.1	24.4	67.2	39.2	41.1	46.5	33.3
Sr (PPM)	86	62	6	37	61	87	23	9
Cd (PPM)	8.2	12.7	7.0	26.9	23.6	22.6	9.4	15.7
Sb (PPM)	11.4	10.3	3.6	12.8	19.6	48.1	5.9	6.7
Bi(ppm)	174	530	334	805	468	532	900	511
V (PPM)	1.78	4.14	1.06	3.37	5.17	7.56	2.01	1.94
Ca (%)	67.4	16.6	1.9	42.6	18.6	19.3	1.8	3.2
P (%)	0.6	0.5	1.1	0.5	0.1	0.3	0.3	0.7
La (PPM)	5.0	1.9	1.0	0.7	4.7	4.5	0.9	1.5
Sc (PPM)	0.6	1.9	1.8<0.02	1.9	2.1	1.3	1.4<0.02	2.3<0.02
Tl (PPM)	0.06	0.05	-	0.08	0.37	0.04		
S (%)	1.57	0.62		0.27	2.24	3.12<5	0.03	
Hg (PPB)	37	6	9<0.1	6	24		6<0.1	9<0.1
Se (PPM)	1.5	0.6	-	0.1	1.6	1.7	-	-
Te (PPM)	0.52	0.11		0.03	0.33	0.38	--	-
Ga (PPM)	0.8	4.1	3.5	3.4	4.4	3.3	4.2	5.0
Cr(PPM))	1.6	13.3	17.9	36.2	21.9	6.5	7.4	22.8
Mg (%)	0.27	1.10	0.49	0.48	1.19	1.15	0.78	0.87
Ba (PPM)	15.8	43.7	51.0	37.6	34.7	24.2	17.1	60.5
Ti (%)	0.108	0.020<1	0.040<1	0.040	0.073	0.009<1	0.017<1	0.057<1
B (PPM)	-	-	-	2	2	-	-	-
Al (%)	0.39	1.75	0.63	1.90	2.87	1.63	1.10	1.24
Na (%)	0.005	0.017	0.032	0.047	0.102	0.007	0.016	0.049
K (%)	0.13	0.13<0.1	0.04	0.20	0.42	0.14<0.1	0.04	0.04
W (PPM)	0.6	0.3	0.2	0.3	0.3	0.1	0.1	0.2

Sample #13-08 and #14Y-08 – pyrite-quartz-sericite-chloritic shale from the river Stori canyon;
 #14W-08 – quartz-sericite-chloritic shale from the river Stori canyon; #15-08- pyrite-quartz-sericite-chloritic shale from the river Stori canyon; #16-08 Silicified clay-shale from the river Stori canyon; #18-09 – oxidized clay- shale from the river Makhvali canyon;
 #38-08 – Silicified plagiogranite from Speroza Massif; #41-09-close-grained xenolith from the river Makhvali “sandstones”.

we may assume that the studied ore elements are genetically connected with deep mantle sources. If this is the case, then these ore lodes must occur at considerable depths. The Stori canyon hydrothermal alterations are also possible and ore mineralization is connected with mantle plume activity, conditioning continental lithosphere thinning, change of its chemical content and other significant geological transformations in this region.

Thus, fractured, cataclastic and mylonitized Lower Jurassic clay-shales at more than 3 km distance undergo

intensive hydrothermal silicification, carbonization and sulphide mineralization.

The entire complex of rocks in this process of hydrothermal alteration was enriched with thorium and bismuth up to industrial concentration (Th-100-200 g/t; Bi-200-900 g/t). This enrichment was especially intensively revealed in quartz-pyrite-pyrrhotine-copper pyrite veins, where the content of these elements reaches the level of world class deposits (Th-3842 g/t; Bi-4806 g/t).

We strongly believe that this discovery is of signifi-

cant strategic and economic value, hence hydrothermally altered Lower-Jurassic clay-shales of the Stori canyon need further urgent detailed study.

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¹ სამიო კომპანია “ოქროს საწმისი”, ლეოვის ქ.36, თბილისი

(წარმოდგენილია აკადემიის წევრის მ. თოფჩიშვილის მიერ)

კავკასიონის სამხრეთ ფერდზე, კახეთში, მდ. სტორის ხეობა აშიშვლებს დამსხვრეულ, კატაკლაზირებულ და მილონიტიზირებულ ქვედაიურულ თიხა-ფიქლებს, რომლებიც 3კმ-ზე მეტ მანძილზე განიცდიან ინტენსიურ პიდროთერმულ გაკვარცებას, გაკარბონატებას და სულფიდურ მინერალიზაციას. ეს პროცესი განსაკუთრებით ინტენსიურადაა გამოვლენილი ბრეჩირების ზონებში, სადაც ზოგჯერ ფორმირდება მძლავრი სულფიდური მადნიანი ძარღვები. ჩვენს მიერ ჩატარებულმა კვლევებმა აჩვენა, რომ ქანების მთელი ეს კომპლექსი პიდროთერმული შეცვლის აღწერილ პროცესში გამდიდრდა სამრეწველო კონცენტრაციამდე თორიუმით და ბისმუთით (Th-100-200 გ/ტ; Bi-200-900 გ/ტ). ეს გამდიდრება განსაკუთრებით ინტენსიურად გამოვლინდა კვარც-პირიტ-პიროტინ-ქალკოპირიტულ ძარღვებში, სადაც ამ ელემენტების შემცველობა მსოფლიო კლასის საბადოების დონეს აჭარბებს (Th-0.3842%; Bi-0.4806%) (თორიუმის და ბისმუთის ქიმიური ანალიზები ჩატარდა კანადაში, ვანკუვერის “ACMELABS” ლაბორატორიაში ICP-OSL მეთოდის გამოყენებით).

ავტორებს მიაჩნიათ, რომ ამ აღმოჩენას მნიშვნელოვანი სტრატეგიული და ეკონომიკური ღირებულება გააჩნია, რის გამოც სტორის ხეობის პიდროთერმულად შეცვლილი ქვედაიურული თიხა-ფიქლები შემდგომ გადაუდებელ დეტალურ შესწავლას საჭიროებს.

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