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NATIVE METALS IN PYRITE ORES OF THE LESSER CAUCASUS

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Abstract

Sample analysis using emission spectral analysis (ESA) on a UBI-2 universal generator with electronic control, local X-ray spectral analysis using a Stereoscan C-4 electron microscope and an MS-46 microanalyzer (France's Cameka) and an IXA-50A Jeol (Japan) allowed us to establish the quantitative and qualitative composition of minerals. X-ray microanalysis was performed on a URS-50I system in an RKD chamber using FeKα radiation. In the study of ore-forming minerals, an LMA-10 laser microspectrometry system (Carl-Zeiss, Jena) with a ruby resonator, passive Q-modulator, and PGS-2 diffraction spectrograph with a quartz cylindrical lens was used for the first time. The elemental composition of several new minerals was determined.

Keywords: *quartz, X-ray, silver, gold formations, hypergene zone, metacolloidal pyrite.*

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Introduction:

Native metals are represented by gold and silver in the primary ores and copper in the oxidation zone of the deposit.

Gold is the main useful component of the ores studied. In hypogene ores, its release is closely associated with the quartz-pyrite (pyrite) and quartz-gold-telluride stages, while in the hypergene zone, it is part of the quartz-gold-goethite-hydrogoethite association [2]. The main gold concentrator of the quartz-pyrite stage is pyrite, represented by massive and breccia formations, in which gold in the form of irregular, isolated aggregates (0.14x0.06 mm) develops along the marginal parts of the crystalline-granular early pyrite (I) and fills its cracks, forming vein-like precipitates against the background of the latter. Isometric inclusions of gold with sizes from 0.007x0.015 mm to 0.05x0.035 mm in cross section are also observed in the interstices of metacolloidal pyrite (I). The most gold-bearing are fine- and medium-grained varieties of early pyrite (I), as well as metacolloidal varieties of pyrite (II) of the pyrite stage, with a predominance of finely dispersed gold formations of light yellow hues, the reflectivity of which fluctuates within the range of 62.8-79.6% (Table 3.3). Results of X-ray diffraction analysis of gold and associated minerals (sample G-18), similar to the reference data (V.I. Mikheev) [3], are not presented in Table 1.1.

Vein-shaped and isometric gold segregations of the gold-telluride stage are observed exclusively in intergrowths with hessite, forming a subgraphic structure with dimensions of 0.01 x 0.05 mm and 0.06 x 0.03 mm. Native gold, in association with hessite and petzite, often creates intergrowth structures against a background of pyrite. Frequently, in certain areas of intensely crushed pyrite, its cracks are healed by minerals of the petzite-hessite-telurobismuthite association, creating overall microloop formations. In the surface and near-surface areas of ore zones, gold tellurides are destroyed, and the gold contained in them is restored to a native state in the form of point (mustard gold), worm-like, spongand mossy segregations of a pale yellow color with greenish and reddish hues, caused by the presence of various trace elements—primarily copper and silver.

Table 1.1.

Results of X-ray analysis of minerals

№	**Sample G-18**		**pyrite**		**gold**		**hessite**	
	I	**d** $_{\alpha/n}$	**I**	**d** $_{\alpha/n}$	**I**	**d** $_{\alpha/n}$	**I**	**d** $_{\alpha/n}$
1	1	7,031	-	-	-	-	0,5	7.,12
2	1	4,494	-	-	-	-	1	4,52
3	0,6	3,509	-	-	-	-	0,5	3,63
4	1	3,336	-	-	-	-	0,5	3,34
5	2	3,123	4	3,128	-	-	5	3,06
6	9	2,704	9	2,709	-	-	8	2,83
7	6	2,418	7	2,423	10	2,35	10	2,30
8	5	2,209	5	2,212	-	-	2	2,18
9	0,5	2,011	-	-	9	2,03	1	2,00
10	4	1,911	4	1,915	-	-	1	1,950
11	10	1,631	10	1,633	-	-	-	-
12	2	1,562	2	1,564	-	-	1	1,541
13	2	1,500	2	1,502	-	-	-	-
14	3	1,445	7	1,445	8	1,437	2	1,443
15			6	1,243	9	1,23	1	1,243
16			1	1,211	-	-	-	-
17			0,8	1,182	-	-	1	1,187
18			0,6	1,155	-	-	-	-
19			0,6	1,106	-	-	-	-
20			3	1,043	-	-	-	-
21			0,8	1,006	-	-	-	-
22			0,6	0,989	-	-	-	-
23			1	0,958	-	-	-	-

24			6	0,903	7	0,933	-	-

The analysis was performed using a URS-50I setup in an RKD chamber with FeKα radiation, in the laboratory of the Central Research Institute of Geology and Mineralogy of the Russian Federation.

Late (hypergene) gold is characteristic of the oxidation zone of the deposit and manifests itself as colloform goethite-hydrogoethite formations that completely replace pyrite aggregates. Here, gold forms both emulsion-like inclusions in goethite and hydrogoethite, as well as relatively coarse-grained segregations that form small intergrowths with these minerals. Filamentous gold segregations are often observed within goethite aggregates; these segregations, often branching, cut these minerals in various directions. Less frequently, euhedral gold grains of pentagonal cross-section, developing through pyrite, are found in oxidized ores. Thus, gold from the oxidation zone is characterized by relatively large grains, increased reflectivity from 81.4 to 88.2% (Table 3.2), and a bright yellow color, unlike hypogene gold. The results of chemical, microprobe, emission-spectrometry analyses of gold from the three above-mentioned associations showed the presence of the following elements in the samples (%): 1) Gold associated with sulfides: Au - 93.03; Ag - 6.13; Fe - 0.26; Cu - 0.005; Sb - 0.005; Bi - 0.005; Te - 0.03; Se - 0.003 and As - 0.009. Undissolved residue - 0.58. 2) Gold associated with tellurides: Au - 84.14; Ag - 14.85; Fe - 0.024; Cu - 0.01; Sb - 0.005; Bi - 0.005-0.01; Te - 0.06; As - 0.004; Se - 0.002; undissolved residue - 0.47. 3) Gold associated with goethite and hydrogoethite: Au - 95.3; Ag - 5.00; Fe - 0.051; Cu - 0.005; Te - 0.02; As - 0.001; Sb - 0.005; Bi - 0.005 and undissolved residue - 0.26. Thus, gold formed during the oxidation of sulfides and tellurides and located in close association with goethite-hydrogoethite aggregates has a high fineness.

When comparing the obtained data, it is evident that the silver content in the quartz-gold-telluride stage is significantly higher than in the pyrite (quartz-pyrite) stage. The increased iron content is due to the presence of surface films of iron hydroxides on gold grains, and tellurium - to the preservation of the remains of its minerals during oxidation. Variations in the contents of other elements are insignificant. Thus, gold fineness is determined by the formation temperature of gold-sulfide deposits, low silver-to-gold ratios [4], and the mineral composition of the ores (gold and silver sulfides and tellurides). The decomposition of these ores removes a number of elements, increasing the fineness of the gold, leaving behind high-fineness supergene gold. All these issues are discussed in more detail in subsequent subchapters.

Silver in the deposit is associated with gold and tellurides and is less commonly found as electrum. Pyrite, galena, sphalerite, tennantite, tetrahedrite, and chalcopyrite are associated with these two noble metals. Native silver of the gold-telluride stage occurs as dendrites, irregular grains, isometric grains, and wire-like grains [1]. In the gold-goethite-hydrogoethite association, silver is closely intergrown with tiny gold grains, often filling cracks in iron hydroxides formed during oxidation, and less commonly as thin inclusions, framing isometric gold segregations within the overall colloform mass, as demonstrated at other deposits. Reflectivity measurements and X-ray diffraction analysis results for silver and associated minerals are presented in tables 1.2 and 1.3.

Table 1.2

Reflectance measurement data (Rm%) for gold, silver and electrum (based on data from A.I. Makhmudov)

mineral	**\\\\ R values (%) for different wavelengths (nm)**														
	440	**460**	**480**	**500**	**520**	**540**	**560**	**580**	**600**	**620**	**640**	**680**	**700**	**720**	**740**
gold	36,0	38,6	44,0	52,6	62,8	72,4	75,8	78,2	79,6	81,4	83,8	85,8	86,4	80,8	88,2
silver	90,2	82,8	83,4	94,0	94,8	95,7	96,2	96,8	97,0	97,4	97,0	98,2	98,6	98,8	98,4
elektrum	63,6	65,7	68,7	73,3	78,8	84,5	86,0	87,5	88,3	89,4	90,1	92,0	92,8	93,6	94,8

The measurements were carried out on FME-2 in the physical-chemical laboratory.

As a result of sampling conducted across the strike of ore zones at various horizons, we found that the gold-to-silver ratio (K) increases with depth, varying within the range of 1:3 - 1:2, and in the host rocks, 1:11 - 1:10. At other deposits in the Lesser Caucasus, this ratio is 1:10 and 1:8 (Vezhnali, Gyzyl Bulag, Tutkhun, etc.).

These data, on the one hand, can serve as a search criterion for finding precious metals in future prospecting and evaluation work, and on the other hand, they properties, precipitates primarily in the quartz-gold-telluride stage, which explains the low gold fineness of this stage.

Table 1.3

Results of X-ray diffraction analysis of some minerals (according to the author)

№	**Sample G-15**		**pyrite**		**cuartz**		**Silver**		**goethite**	
	I	**d $_{\alpha/n}$**	**I**	**d $_{\alpha/n}$**	**I**	**d $_{\alpha/n}$**	**I**	**d $_{\alpha/n}$**	**I**	**d $_{\alpha/n}$**
1	1	10,086	-	-	-	-	-	-	-	-
2	0,8	7,132	-	-	-	-	-	-	-	-
3	0,7	5,901	-	-	-	-	-	-	-	-
4	0,9	5,075	-	-	-	-	-	-	-	-
5	9	4,199	-	-	5	4,257	-	-	10	4,183
6	6	3,346	-	-	10	3,342	-	-	3	3,383
7	2	3,129	2	3,128	-	-	-	-	-	-
-	0,7	3,079	-	-	-	-	-	-	-	-
9	1	2,974	-	-	-	-	-	-	-	-

10	8	2,704	8	2,709	-	-	-	-	8	2,693
11	1	2,569	-	-	-	-	-	-	1	2,583
12	2	2,497	-	-	-	-	6	2,500	2	2.489
13	7	2,452	-	-	5	2,457	-	-	9	2,450
14	7	2,420	7	2,423	-	-	10	2,425	-	-
15	4	2,278	-	-	4	2,282	-	-	-	-
16	7	2,209	7	2,212	-	-	-	-	-	-
17	2	2,192	-	-	-	-	-	-	3	2,190
18	5	2,119	-	-	5	2,127	-	-	-	-
19	7	1,996	-	-	-	-	8	2,050	-	-
20	6	1,916	6	1,915	-	-	-	-	2	1,920
21	7-8	1,813	-	-	8	1,818	-	-	4	1,802
22	5	1,721	-	-	-	-	-	-	5	1,719
23	1	1,668	-	-	4	1,672	1	1,666	1	1,659
24	9	1,633	10	1,633	-	-	-	-	-	-
25	2	1,562	2	1,564	-	-	1	1,561	3	1,564
26	1	1,541	-	-	1	1,542	-	-	-	-
27	3	1,501	3	1,502	-	-	-	-	3	1,509
28	8	1,446	6	1,445	-	-	10	1,443	-	-
29	2	1,373	-	-	1	1,372	-	-	3	1,369
30	3	1,242	3	1,243	-	-	10	1,240	1	1,244
31	5	1,178	2	1,182	-	-	5	1,170	-	-

The analysis was performed using a URS-50I setup in an RKD chamber with FeKα radiation, in the laboratory of the Central Research Institute of Geology and Mineralogy of the Russian Federation.

Copper. At the Goshinskoye deposit, dendritic small aggregates of native copper are noted in the oxidation zone of the sublatitudinal (№ 5) and submeridional (№ 10 and 13) zones, where it sometimes contains up to 2.5% iron and inclusions of native silver. Golden copper contains up to 2-3% gold. It occurs in association with cuprite, iron hydroxides, and other hypergene copper minerals. Copper. At the Goshinskoye deposit, dendritic small aggregates of native copper are noted in the oxidation zone of the sublatitudinal (№ 5) and submeridional (№10 and 13) zones, where it sometimes contains up to 2.5% iron and inclusions of native silver. Golden copper contains up to 2-3% gold. It occurs in association with cuprite, iron hydroxides, and other hypergene copper minerals. Copper. At the Goshinskoye deposit, dendritic small aggregates of native copper are noted in the oxidation zone of the sublatitudinal (№ 5) and submeridional (№ 10 and 13) zones, where it sometimes contains up to

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The obtained results of studying the composition of pyrite ores at several deposits in the northeastern Lesser Caucasus allow us to draw the following conclusions:

1. A consistent pattern of ore types has been established within the ore body contour. Vein-disseminated pyrite formations in metasomatites are developed in the footwall of the ore body. Above these, massive ores are observed, the textures of which alternate in the following order: crystalline-granular with features of banded structures; crystalline-granular fine-banded; fine-grained ores with widespread development of colloform formations and areas of banded formations.

2. Hypogene gold (medium fineness) is mainly found in crystalline-granular and cataclastic structures, while hypergene (high-fineness) gold is found in corroded and skeletal structures, respectively, in massive and breccia ore textures.

3. The ore formation process begins with the formation of a pyrite-sulfide (quartz-pyrite) association with gold, followed by quartz-polysulfide, quartz-gold-telluride, and less common quartz-carbonate associations. The process ends with the deposition of oxidized ores, which include the productive quartz-gold-goethite-hydrogoethite association.

4. The release of gold and silver from hydrothermal solutions occurred throughout the ore formation process, but the most productive stages are: hypogene – pyrite-sulfide (quartz-pyrite) and quartz-gold-telluride, as well as supergene quartz-gold-goethite-hydrogoethite, where they are present in both native and finely dispersed forms.

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