

Pyrite from Zones of Mz-Kz Reactivation of Large Faults on the Eastern Slope of the Ural Mountains, Russia

O. B. Azovskova, A. A. Malyugin, A. A. Nekrasova, and M. Yu. Yanchenko

Abstract—Pyritisation halos are identified in weathering crusts and unconsolidated formations at five locations within large fault structure of the Urals' eastern slope. Electron microscopy reveals the presence of inclusions and growths on pyrite faces – normally on cubic pyrite with striations, or combinations of cubes and other forms. Following neogenesis types are established: native elements and intermetallic compounds (including gold and silver), halogenides, sulphides, sulfosalts, tellurides, sulphotellurides, selenides, tungstates, sulphates, phosphates, carbon-based substances. Direct relationship is noted between amount and diversity of such mineral phases, and proximity to and scale of ore-grade mineralization. Gold and silver, both in native form and within tellurides, presence of lead (galena, native lead), native tungsten, and, possibly, molybdenite and sulfosalts can indicate gold-bearing formations. First find of native tungsten in the Urals is for the first time – in crystallised and druse-like form. Link is suggested between unusual mineralization and “reducing” hydrothermal fluids from deep-seated faults at later stages of Urals' reactivation.

Keywords—Gold in weathering crust, low temperature metasomatism, pyrite, native tungsten, Urals.

I. INTRODUCTION

A large number of partially depleted gold and gold-bearing deposits and mineralization is associated with the junction of the two largest structures of the Urals' eastern slope - Tagil and East Urals mega zones (see Fig. 1) [1]. Thanks to the advance of gold ore production and processing technology, comprehensive exploration and re-evaluation of those assets is back on the agenda, as well as the identification of further prospective areas with potential commercial targets.

This part of the Urals is largely “concealed” under a blanket cover of unconsolidated sediments and weathering crusts, often quite thick. The most effective way of prospecting in such conditions is by means of various panning methods supported by different mineralogical studies.

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Over the last decade application of these techniques in prospecting for lobe gold, placer gold, and gold-bearing weathering crusts allowed to identify late pyritisation halos within complex structures at the junction of Tagil and East Uralian mega zones (Serovsko-Maukski deep-seated fault and its echelon faults, Mramorsk and Yemekh shear zones etc.) [2], [3]. By now such halos have been mapped in Mramorsk (Mr), Krasnouralsk (Kr), North Krasnouralsk (SKU) blocks, in the area of Bogomol (Bg) gold deposit, and in Gumesheki (Gum) gold-bearing skarn copper deposit (see Fig. 1). They measure from 200 m to over 1km in width. Pyrite halos are closely associated with signs of low-temperature metasomatism, and spatially often tend towards zones of fault carbonisation [3], [4].

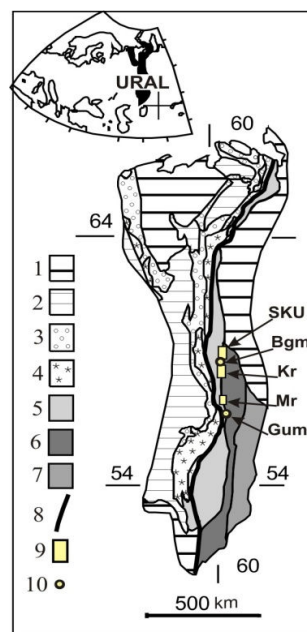


Fig. 1 Location of sites within structures of the Urals 1 – Mesozoic – Cenozoic deposits; 2 – Pre-Uralian foredeep; Megazones (3-7): 3 – West Uralian, 4 – Central Uralian, 5 – Tagil and Magnitogorsk, 6 – East Uralian, 7 – Transuralian; 8 – Main Uralian Deep Fault; areas of research (9, 10): 9 – prospective blocks (SKU – North Krasnouralsk, Kr – Krasnouralsk, Mr – Mramorsk), 10 – deposits (Bgm – Bogomol, Au; Gum – Gumesheki, Au-Cu)

The “Young” (Meso-Cenozoic) age of pyrite mineralisation is defined by its occurrence in the upper section, where

weathering crusts of the chemical section are Upper Mesozoic [5], and unconsolidated overlying formations are dominated by Neogene-Quaternary continental deposits.

The purpose of the research is to explore typomorphic features of pyrite and related mineralisation within "reactivated" fault structures. Key objectives are: 1) to identify the relationship between "young" mineralisation and endogenic ore-grade mineralisation processes; 2) to identify patterns which could be used as criteria and indicators in prospecting practice.

II. DATA AND METHODOLOGY

The research is based on prospecting and exploration data from five sites: Mramorsk, Krasnouralsk, and North Krasnouralsk blocks; Bogomol, and Gumeshki deposits (see Fig. 1). Prospecting included mapping of unconsolidated Mesozoic-Cenozoic sediments and weathering crusts, along with extensive panning (~ 2-5 thousand samples from each site). Following magnetic and electromagnetic separation samples were inspected under the binocular microscope to record any presence of "fresh" sulphides (pyrite, pyrite + marcasite) and visually assess their quantity using following scale: single or occasional signs – signs – many signs – abundance. Pyrite crystallography analysis was performed on typical samples within the halos. Surfaces of pyrite grains (non-polished samples, natural faces) from all sites were extensively studied using Jeol electron scanning microscope JSM-6390LV with EMF-microanalyser. Some samples were tested for pyrite surface composition using Auger electron spectroscopy (AES) and the Riber LAS-3000 unit. Details of methodology are provided in [4]. Pyrite geochemistry was studied using ICP-MS technique in Perkin Elmer ELAN-9000 mass-spectrometer with inductively-coupled plasma. Monomineral fractions of certain morphological types were analysed for North Krasnouralsk, Krasnouralsk, Mramorsk blocks. Details of the method and results of geochemical studies are provided in [2], [6].

III. RESULTS AND DISCUSSION

SEM studies of pyrite face surfaces in secondary and back-scattered electrons reveal frequent presence of inclusions and growths of various mineral phases - and rather exotic ones in some cases. This mostly applies to cubic pyrite with strong striations, or to combinations of cubes with other forms. In terms of their composition inclusions and growths can be divided into several groups: native elements and intermetallic compounds (including gold and silver), halogenides, sulphides, sulfosalts, tellurides, sulphotellurides, selenides, tungstates, sulphates, and phosphates. Each pyrite grain can be associated with one or several mineral phases. The most diverse set of microinclusions and growths is observed in samples collected from known or assumed gold ore assets (Bogomol, Gumeshki deposits, certain parts of Mramorsk and North Krasnouralsk blocks). However, in each case the set has its own distinctive features.

A. Mramorsk Block

Crystallomorphological analysis identifies several pyrite varieties which may be present in samples either separately or in any combination. The early generation presumably includes cubic, sometimes druse-like, greyish-yellow and brass-yellow pyrite-I with clear striations. Grain size from $n \times 0.01\text{mm}$ to 0.5mm , occasionally larger. The later pyrite-IV features distinctive poorly expressed faces and smoothed edges. It is normally cubic, or, less often, a combination of cube and pentagon-dodecahedron, usually not larger than few hundredths of a millimeter in size. Two other varieties (fine pyrite-II with its complex forms, and aggregative grey pyrite-III) have minor presence. Pyrite-I occurs predominantly within gold-bearing zones (gold anomalies), while pyrite-IV occurs in their outer haloes. Electron microscopy of pyrite-I grains from weathering crusts of the most promising gold anomaly reveals various mineral phases on its surfaces: gold, electrum, hessite, petzite, Au-Pb-Ag phase, Pb-Ag-Te phase, altaite, tellurobismuthite, native tungsten, native tin and silver-lead, molybdenite. The most common of those are tellurides and molybdenite (see Fig. 2).

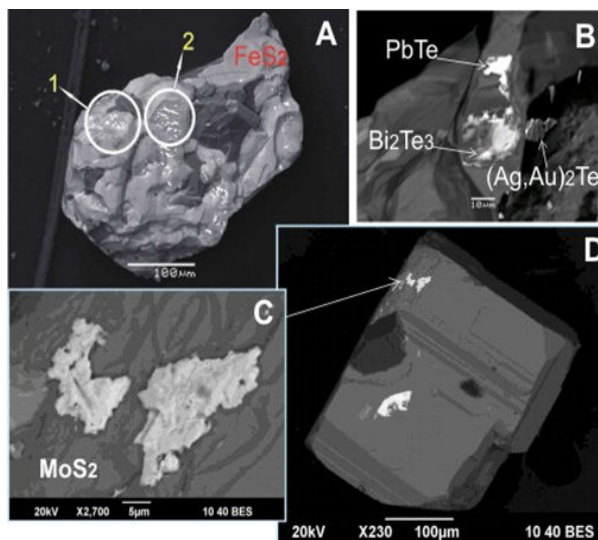


Fig. 2 Typical mineral phases observed in pyrite of Mramorsk block (A) circle 1 – hessite Ag_2Te , petzite AgAuTe_2 , electrum, Au-Pb-Ag phase (A) circle 2 – hessite Ag_2Te , silver-lead Pb(Ag) , Pb-Ag-Te phase (B) altaite, tellurobismuthite, and petzite (C),(D) molybdenite

ICP-MS data on monomineral fraction of this pyrite from one of the samples feature sharply anomalous concentrations (ppm): Mo (13,600), Au (48), Ag (824), Pb (1,203), Bi (1,780), Te (714), while arsenic content (58) is 1-2 orders of magnitude lower than normal for gold-ore and gold-bearing systems [7], [8]. Morphologically similar pyrite on the periphery of ore-bearing zone has clear surfaces, often contains micro-inclusions of chalcopyrite, sometimes sphalerite and arsenopyrite, and they correspond to high content of Cu (ppm) (90,434), As (2,198), Zn (3,718). Pyrite on the periphery of gold-bearing zone, and pyrite-IV are gold-poor – $0.4 \pm 0.1\text{ppm Au}$, which is typical for outer haloes of gold

ore systems [7].

B. Krasnouralsk and North Krasnouralsk Blocks

Halos of neogenetic pyrite in these blocks are controlled by sutures of Serovsko-Maukski deep-seated fault and its branches. However, areas of abundance of such pyrite normally fall within AAS-determined Au anomalies, and spatially align with clear signs of low temperature metasomatism. Dominant morphological types of pyrite in Krasnouralsk block are cubes and cube-pentagon dodecahedron combinations, in North Krasnouralsk block – cubes and octahedrons, and they normally occur separately both in plan and in section. Inclusions and growths on pyrite surfaces are relatively rare, they are associated with grains of cubic and combined form, and mostly limited to chalcopyrite. More diverse and exciting set of inclusions was found in samples from areas of known targets and prospective gold anomalies. In Krasnouralsk block such inclusions are represented by chalcopyrite, galena, sphalerite, and native copper and tin, in North Krasnouralsk block – by chalcopyrite, galena and selenium galena, native lead and tungsten, barite, carbon-based substance. Previous research into geochemistry of such pyrite in these blocks indicates their probable association with gold ore system halos of various degrees of proximity [2], [6].

Micromineralogical research was particularly focused on known and partially depleted (primary ore) Gumeski and Bogomol deposits, where commercial gold had been recently established in up to 100 m thick “crust-argillization” part of the section– in early 1990’s in Gumeski, and in 2009-12 in Bogomol.

C. Gumeski Deposit

It has been known for several millennia, and mostly produced copper (primary and oxidized ore) and malachite. Prospecting and research conducted here by the authors (O. B. Azovskova, A. A. Malyugin) identified extensive low temperature metasomatic processes (argillization, jasperoidisation) with characteristic quartz-kaolinite-pyrite paragenesis along gold ore-grade mineralization. This mineralization can be classified as an unconventional supergene-hypogene type associated with the time of Mesozoic tectonic and plutonic reactivation [9], or with the final stage of development of a single porphyry copper system [10].

Morphometry of pyrite from unconsolidated part of the section shows dominance of cubic forms (with or without striations), some cube-octahedron combinations, dodecahedrons, and occasional icosahedrons. Grain size normally does not exceed 1mm. 117 pyrite grains from 12 samples collected from different depths – 2-2.5m to 148m – were studied under electron microscope. Inclusions, interpositions, growths of various mineral phases were found in 88 grains. The summary is shown below in Table I.

As it is mainly a copper deposit the most frequent finds are chalcopyrite and secondary copper sulphides (bornite, chalcocite, covellite, often mixed together). Among other

inclusions and growths the most common are zinc-bearing grey copper ore (see Fig. 3), lead minerals – native lead and galena, including selenic galena (up to clausthalite, PbSe), and native tungsten.

TABLE I
TYPES OF MINERAL INCLUSIONS AND GROWTHS ON THE SURFACE OF PYRITE FROM WEATHERING CRUST AND ARGILLITE OF BOGOMOL AND GUMESKI DEPOSITS

Group	Bogomol	Gumeski
	Mineral types	
Native metals and intermetallic compounds	copper , zinciferous copper, gold (incl. mercuriferous), silver, iron, lead , tungsten	copper, gold (incl. mercuriferous), iron, lead , tin, tungsten
Halogenides	-	Bromargyrite, iodargyrite
	Galena and selenium galena, chalcopyrite , and secondary copper sulphides, sphalerite, alloyite, cobaltite , bismuthine	Galena and selenium galena, chalcopyrite, and secondary copper sulphides, molybdenite , sphalerite,
Sulphides		
Tellurides and sulfo-tellurides	coloradoite (HgTe), tellurium palladite (PdTe), tetradymite	-
Selenides	Ag-Se(+Cu) phase (naumanite?)	-
Sulphosalts and similar undefined phases	Zinciferous tennantite-tetrahedrite (sandbergite)	Zinciferous tennantite-tetrahedrite (sandbergite), Hg-Cu-Zn-Cd-S (\pm Fe, Co, Cl, Br) phases, Fe-Cu-Pb-S phase
Tungstates	-	Scheelite
Sulphates	Barite	-
Phosphates	Monazite	Monazite, F-apatite
Associated mineralisation	Native: gold, aluminium, zinciferous copper, cupriferous silver; arsenopyrite, cobaltite, alloyite-glaucodot, carbon-based substance (bitumen, suspended carbon substance)	Native copper, native gold, arsenopyrite, graphite

Most common phases are shown in bold

Relatively common are inclusions of molybdenite (see Fig. 3 (A)) and gold. Inclusions of a complex and unusual mercuriferous phase Hg-Cu-Zn-Cd-S (\pm Fe, Co, Cl, Br) were identified in 4 grains – all from the same sample, however. Among single or occasional inclusions are native copper, tin and iron arsenopyrite, halogenides (bromargyrite, iodargyrite), unidentified Pb-Cu-S phase, scheelite, as well as monazite, fluor apatite, inclusions and patches of carbon-based substance.

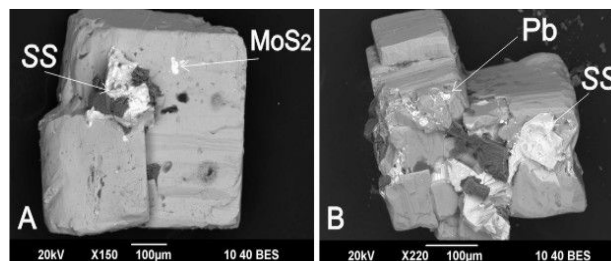


Fig. 3 Growths of Zn-containing grey copper ore (SS), inclusions of molybdenite (A) and native lead+anglesite? phases (B) on surfaces of pyrite grains, Gumeski

D. Bogomol Deposit

It is still in the early stage of contemporary exploration phase. Until 20th Century it was intermittently mined for gold-bearing quartz veins. In recent years commercial gold in the form of mineralised zones and linear stock works has been identified there. A range of data suggests significant role of low-temperature mineralisation and metasomatic processes in development of this deposit. The same is indicated by micromineralogy of pyrite from weathering crust associated with low-temperature metasomatites. Pyrite grain morphology is dominated by cubes and cube-based combined forms. 151 grains from 27 samples collected from various locations within the ore field from depths of under 1m – 86m were studied under electron microscope. Various inclusions and growths categorised in Table I were found in 98 grains. The most common phases include native tungsten, galena and selenic galena, chalcopyrite. Not uncommon also are inclusions of native lead, gold and copper, cobaltite, alloclasite, barite, monazite. There are rare inclusions of native silver and iron, while the remaining mineral types occur only occasionally.

The most interesting are finds of native tungsten (see Fig. 4).

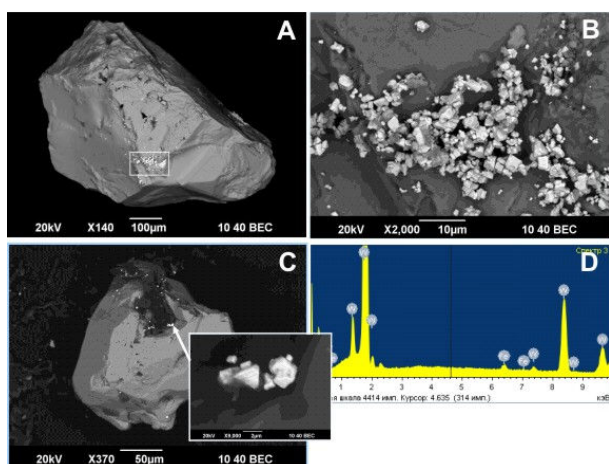
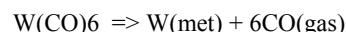


Fig. 4 Native tungsten on pyrite (Bogomol deposit) (A), (B) druse-like growths (C) native tungsten on the periphery of bitumen inclusions (dark area) (D) example of energy dispersive spectrum of one of the tungsten grains

By now this rare mineral type has been found in exhalative products of the Great Tolbachik Fissure Eruption, in ores of Sukhoi Log deposit, and in oil and gas formations of Dnieper-Donets Depression and Middle Ob Basin [11], [12]. We were the first to find native tungsten in the Urals and for the first time were it found in a well crystallised and druse-like form. The fact that it occurs in pyrite halos of all blocks covered by this research, except Krasnouralsk Block, indicates a clear pattern of its development in zones of Meso-Cenozoic reactivation of faults. A link between tungsten and segregations of carbon substance (bitumen) of fluid origin (see Fig. 4) can also often be observed. While considering possible

mechanisms of native tungsten development in low-temperature near-surface conditions [13], [14] one has to take the following into account: tungsten compound should be volatile, and breakdown reaction should run at low temperatures. Such conditions are satisfied by, for example, tungsten hexacarbonyl $W(CO)_6$ with boiling point of 175°C, by WF_6 (t. b. 19.5°C), WCl_6 (t. b. 347°C) compounds, as well as by such organic tungsten compounds as $[W(CH_3)_6]$ and $\{W_2[CH_2Si(CH_3)_3]_6\}$, which have melting points of 30°C and 110°C respectively. These compounds are not very resilient and can break down in surface conditions. Tungsten hexacarbonyl is stable at higher pressures, but at lower pressures (relief conditions) it begins to break down even at 50°C [15].



If dissolved in an organic matrix, tungsten hexacarbonyl entering oxygenated environment can get oxidised.



It should be noted that not only the presence of native tungsten, but the development of many mineral types described above can be associated with the involvement of “reduced” hydrocarbon-enriched fluid phases. Active role of organic matter is confirmed by its presence in surrounding metasomatites and tectonites (particularly in Mramorsk, North Krasnouralsk blocks, and Bogomol deposit), and by the results of Auger electron spectroscopy of the pyrite surfaces (detailed results – in [4]). A large number of grains from various locations in Krasnouralsk and North Krasnouralsk blocks was analysed, and ion beam etching revealed anomalously high carbon concentrations in all of them. In one particular case an inclusion was discovered on a pyrite face (covering 10-15% of the face area) which consisted practically of carbon only. Presence of nitrogen on faces of cubic pyrite from several samples is rather interesting, and suggests a strong reducing environment.

New data on mineralogy of pyrite from zones of Meso-Cenozoic reactivation of Urals structures correlate well with the results of recent research into pyrite-controlled gold accumulation [16]. In particular authors note approximately 500 nm thick pyrrhotite-like or marcasite-like nonautonomous phases (NAPs) on pyrite surface which concentrate gold. Changes in physical-chemical environment drive excess Au from NAP structure to create other chemical forms or Au nano- or microparticles [17]. Similar mechanism seems to be applicable to other metals too.

IV. CONCLUSION

The research demonstrated the importance of identification and mapping of pyritization halos in weathering crusts and other unconsolidated formations, both for regional geoscientific studies (improvement of understanding of geological history, and metallogenic forecasts), and for the purposes of prospecting. The quantity and type composition of

micro-inclusions and growths on pyrite surfaces reflect intensity, nature, and sequence of the most recent mineralization processes. This can be an important factor in understanding young (“reactivated”) and multiple-stage ore systems. Further research is needed to identify any patterns. But certain tentative practical conclusions can be made even now: 1) there is an observed direct relationship between quantity and diversity of mineral phases on pyrite grain surfaces, and the proximity and scale of ore-grade mineralization; 2) inclusions of gold and silver in native form and within tellurides, presence of lead phases (galena, native lead), inclusions of native tungsten and, possibly, molybdenite and sulfosalts may indicate proximity of gold mineralization.

Presence of native tungsten may be significant not only as a mineralogical oddity or a local predictive factor. It appears [12] that the presence of native tungsten particles serves as a kind of a tracer of superdeep fluids.

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REFERENCES

- [1] V. N. Sazonov, V. N. Ogorodnikov, V. A. Koroteyev, Yu. A. Polenov, *Urals Gold Deposits*. Yekaterinburg: UGGGA, 2001.
- [2] O. B. Azovskova, K. A. Zubarev, J. L. Ronkin, A. A. Nekrasova, L. O. Magazina, “First data on pyrite geochemistry in zones of Meso-Cenozoic reactivation in the Middle Urals, connection with endogenous gold mineralisation”, in: *Proc. Internat. Conf. Problems of geology of Ore Deposits, Mineralogy, Petrology, and Geochemistry*, Moscow, 2008. pp. 113-117.
- [3] O. B. Azovskova, A. P. Mikhailov, A. A. Nekrasova, A. I. Zubkov, “Development of placer gold ore systems in long-lived deep-seated fault zones (example of Serovsko-Maukski Fault, Middle Urals)” in *Proc. II Intern. Mining and Geol. Forum Gold of North Pacific Margin*, Magadan, 2011. pp. 50-52 (Eng.).
- [4] O. B. Azovskova, Y. V. Schegolkov, S. P. Glavatskih, A. A. Nekrasova, “Pyrite from haloes of reactivation of large fault structures: certain typomorphic features and association with carbon metasomatism”. // *Proc. Intern. Seminar Crystalline and Solid Non-crystalline State of Mineral Substance*, Syktyvkar, 2012. pp. 105-108.
- [5] A. P. Sigov, *Metallogeny of Mesozoic and Cenozoic in the Urals*. Moscow: Nedra, 1969.
- [6] O. B. Azovskova, A. A. Nekrasova, Yu. V. Schegolkov, “Description of “young” pyrite mineralisation of Serovsko-Maukski Fault zone (Aivinsko-Yemekhski block)”. *Bulletin of the Urals Branch of RMS* No. 8, Yekaterinburg. 2011. pp. 5-12.
- [7] B. S. Andreyev, *Pyrite in gold Ore Deposits*. Moscow: Nauka, 1992.
- [8] G. A. Yurgenson, *Typomorphism and Ore Formations*. Novosibirsk: Nauka, 2003.
- [9] O. N. Gryaznov, A. G. Barannikov, K. P. Savelieva, Unconventional types of gold-argillite mineralization in Mesozoic structures of the Urals. // *Izvestiya UGGU*, Iss. 22, pp. 41-53, 2007.
- [10] A. I. Grabezhev, V. I. Sotnikov, A. A. Borovikov, O. B. Azovskova “Genetic Typification of Gumeshki Copper-Skarn Deposit (Middle Urals). // *Reports of the Academy of Sciences*, Vol. 380, No. 2, pp. 242-245, 2001.
- [11] S. F. Glavatskikh, N. V. Trubkin, “First Finds of native Tungsten and Silver in exhalation Products of the Great Tolbachik Fissure Eruption, Kamchatka. *Reports of the Academy of Sciences*, vol. 373-A, no. 6. pp. 1282-1285, 2000.
- [12] A.E. Lukin, “On native tungsten in rocks of petroliferous complexes”, *Reports of the National Academy of Sciences of Ukraine*, 2009, No. 2, pp. 121-130.
- [13] “Organoelemental Chemistry Methods. Copper, Scandium, Titanium, Vanadium, Chromium, manganese Subgroups”, book 2, A. N. Nesmeyanova and K. A. Konenkova, Ed., Moscow: 1974.
- [14] C. B. Pamplin, T. W. Hayton, P. Legzdins, “Tungsten: Organometallic Chemistry”, *Published Online: 15 DEC 2011 DOI: 10.1002/9781119951438.eibc0233. Published in Encyclopedia of inorganic and bioinorganic chemistry*.
- [15] V. E. Ivanov, E. P. Nechiporenko, V. M. Krivoruchko, V. V. Sagalovich, *Crystallisation of High-Melting-Point Metals from Gas Phase*, Moscow: Atomizdat, 1974.
- [16] V. L. Tauson, D. N. Babkin, T. M. Pastushkova et al., *Dualistic distribution coefficients of elements in the system mineral-hydrothermal solution. I. Gold accumulation in pyrite*. *Geochemistry*, No. 6, pp. 295-604, 2011.
- [17] V.L. Tauson, R.G. Kravtsova, “Gold distribution and modes of gold occurrence of pyrites of epithermal gold-silver deposits of Northern Okhotsk region”, in *Proc. II Intern. Mining and Geol. Forum Gold of North Pacific Margin*, Magadan, 2011. pp. 17-19. Engl.