Reflectivity and microhardness of sulfide minerals as genetic information source (case study: pyrite and arsenopyrite)

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Abstract. Reflectivity and microhardness of pyrite and arsenopyrite of black shale gold-ore deposits in Chertovo Koryto (Patom upland) were studied. It was found that sulfides of different generations are characterized by different values of above-mentioned parameters which is associated mechanical and isomorphic impurities.

1. Introduction

Reflectivity is the main quantitative and diagnostic constant of ore minerals which is closely connected with mineral composition and structure. Reflectivity can be measured along one wavelength and across a visible spectrum. The study of reflection the spectrum is more informative, as it indicates the changing reflectivity in relation to the wavelength itself. Both mechanical and isomorphic impurities, as well as ultrafine structure of decomposed solid solutions affect the spectral reflectance curve shape. One and the same element of different accompanying elements could increase or decrease the reflectance. For example, reflectance increases to increasing iron content in oxides [1, 2].

Microhardness parameter is successfully used as a typomorphic indicator for ore (sulfides) and non-metallic (grenades, fluorite, topaz and others) minerals. Based on this parameter minerals are classified to generations and the influence of certain impurities on the microhardness value is also determined [1, 3, 4, 5].

The present paper deals with the study results of reflectivity and microhardness of pyrite and arsenopyrite, being the main ore minerals in Chertovo Koryto gold-ore deposit.

This deposit is located in the north of Patom upland within the Big Patom river basin. Thick (up to 150 m) ore deposit was formed in the early Proterozoic carbonaceous terrigenous slates of Mikhailovskoe suite. The suite embraces metasomatic rocks of beresite-propylite formation with vein-disseminated sulfide-quartz mineralization. Sulfides occur rarely in quartz veins and veinlets. Pyrite, arsenopyrite and pyrrhotite are predominate. Some galena, sphalerite, chalcopyrite, cobaltite, native plumbum, ulmanita, tellurobismuthit, valleriite impurities can be found in the quartz sulfide complexes. Free gold dominates in quartz. A more detailed description of this deposit is given in [6, 7].

2. Research technique

Pyrite and arsenopyrite monomineral samples were selected to study the reflectivity of sulfides. A portion of samples was abraded into powder for the atomic emission analysis in order to determine the impurity element content. The remaining pyrite and arsenopyrite grains were crushed into pieces and

carefully polished to obtain more reliable reflectivity values. Polished sections were also used. Microscope spectrophotometer MSFU-K was applied in measuring the reflectivity. The spectral reflectance curves were recorded in the range from 400 to 750 nm at the sampling rate of 4.0 nm. More than 100 measurements were performed.

The device PMT-ZM with ocular photoelectric micrometer (FOM-2-16) attachment was used in studying microhardness. The indenter was the diamond pyramid Vickers. 30-40 shots were conducted, each of which involved 5 diagonal measurements and further calculation of the mean value. More than 600 shots were performed in 20 samples. Analysis of measurement results was performed on the basis of S. I. Lebedeva method [8] which makes it possible to evaluate the results more objectively. The aim of this method is to find the most probable mineral microhardness value via variation curves. In this case, the microhardness of minerals (kgH/mm^2) was determined on different face sections and the variation magnitude and width of microhardness interval were determined.

Further, measurement occurrence frequency (P, %) was calculated in specified intervals. Finally, variation curves were designed for each sample and the most probable values were identified.

3. Research findings

Based on previous crystallomorphology studies, analysis of polished sections and thermal emf it was established that there are 4 generations of pyrite and 2 generations of arsenopyrite in Chertovo Koryto deposit [9].

Pyrite

Pyrite I – widely spread in the carboniferous area of the metasomatic halo as porphyroblasts (up to 1 cm).

Pyrite II – well- developed within the rock mass as chain clusters of cubic crystals of up to 1 cm with the distinct edges and accompanied by thin quartz-carbonate veinlets.

Pyrite III—well- developed as granular aggregates in quartz veins and embracing a variety of morphological crystal types and different thermal emf parameters: from pyrite I and II generations.

Pyrite IV – formed during the replacement of pyrrhotite, located in quartz and are marcasite-pyrite aggregates. It is developed on the peripheral part of pyrrhotite or along its the cracks.

The first three generations of pyrite could be applied in study of reflectivity and microhardness.

Arsenopyrite

According to mineralographic results 2 generations of arsenopyrite were revealed. Arsenopyrite I found in rocks as short prismatic porphyroblasts. Arsenopyrite II found in quartz veins and veinlets as granular aggregates. The cataclastic texture of arsenopyrite II revealed in the polished sections indicates the fact the mineral grains were crushed and then quartz cemented. Both generations are suitable for studying reflectivity.

As minerals have different optical properties, the approach in studying the reflectivity was different. Optically, pyrite is an isotropic mineral, although there is evidence that in nature anisotropic pyrite exists. The studied pyrite showed no evidence of reflectivity anisotropy. In this case, arbitrary cross-sections were examined. In the case of arsenopyrite it was reverse. Visually, it was very difficult to identify the maximum darkening time of the grain, as it can be more than 5 degrees. To determine this moment visually it was necessary to perform the measurements from the original position of the grain rotating at +5 and -5 degrees. All graphic measurements were compared with reference samples. Reference samples were curves for «pure» pyrites and arsenopyrites imported from http://www.webmineral.com/.
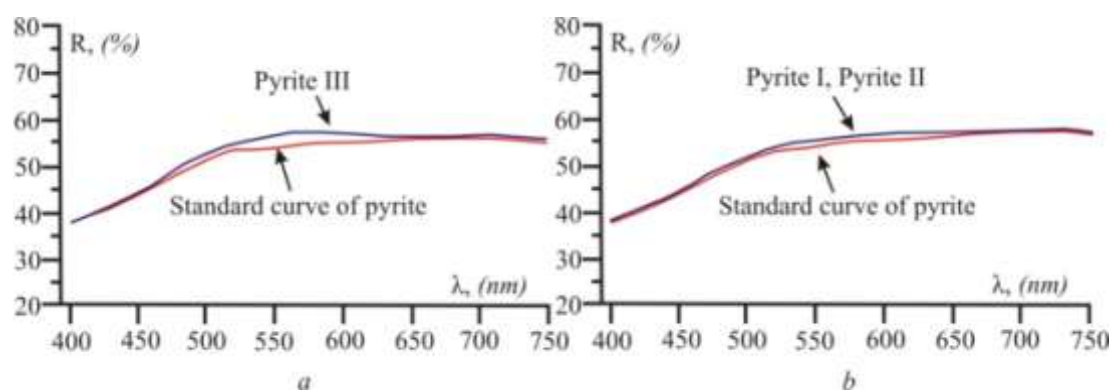
The spectral reflectance curve for pyrite can be seen in Fig. 1. The spectral reflectance curve of the pyrite III (Figure 1, a) differs from the " reference sample" one which is probably due to the high content of Co and Ni in comparison with pyrite I and II (Table 1). According to the previous studies [9, 10] it was found that the typical electronic conductivity of pyrite III is associated with isomorphic Co and Ni impurities. The differences in the spectral reflectance curve of pyrite III and pyrite reference sample are expressed by the reflectivity increase from 53,4 to 57.2% at the wavelength of 540 nm. The spectral reflectance curves of pyrites I and II (Figure 1, b) coincide and they are slightly different from

the reference sample curve at 500...600 nm, which could be explained by the presence of cobalt and nickel. Pyrites have different microhardness parameter (Table 1) which is associated with the presence of Co and Ni. Pyrite III involves increased Co and Ni content, but low microhardness.
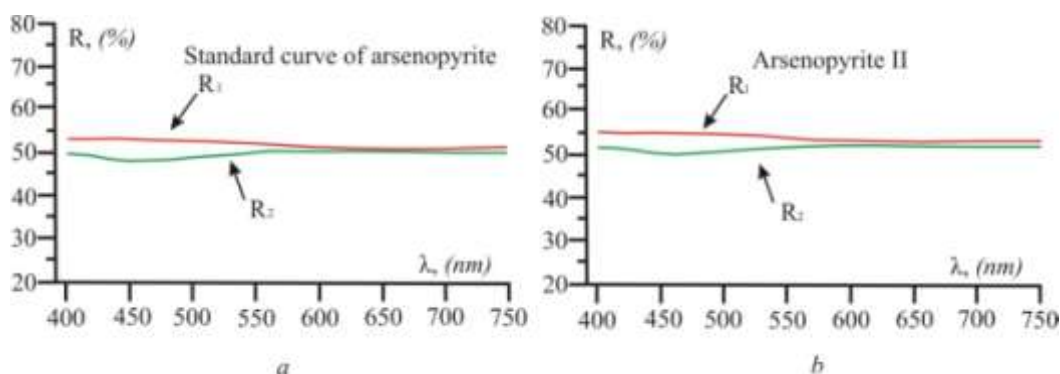
Table 1. Morphological parameters of different pyrite generations.

Minerals	Mean value H, kgH/mm^2	The range of values of the thermal emf, mV	Content Co, g/t (average content)	Content Ni, g/t (average content)
Pyrite I (5 samples)	1500	+(46…64)	23.0-82.1 (44.3)	93.4-268.5 (151.6)
Pyrite II (3 samples)	1580	+(49…58)	26.2-79.3 (31.5)	175.5-290.0 (233.8)
Pyrite III (4 samples)	1400	+(25...67) −(60...67)	150-200 (177.8)	370.7-514.6 (421.6)

The obtained spectral reflectance curves for arsenopyrite are presented in Figure 2. The reflectance spectra of arsenopyrites are non-parallel with very weak dispersion and intersect at 530-580 nm depending on the section. The spectral reflectance curve of arsenopyrite I isn't different from the sample curves (Figure 2, a) and the spectral reflectance curve of arsenopyrite II have the same shape, but they are located below the ordinate axis (Figure 2, b), i.e. the mineral has higher reflectivity values at particular wave length. This can be related to the presence of mechanical impurities of galena in arsenopyrite, which was revealed by using the electron microscope. According to the references the spectral reflectance curve for galena is typical, which is lower at the ordinate axis than for arsenopyrite and at the wavelength of 540 nm the reflectivity is about 44 % [1, 11].

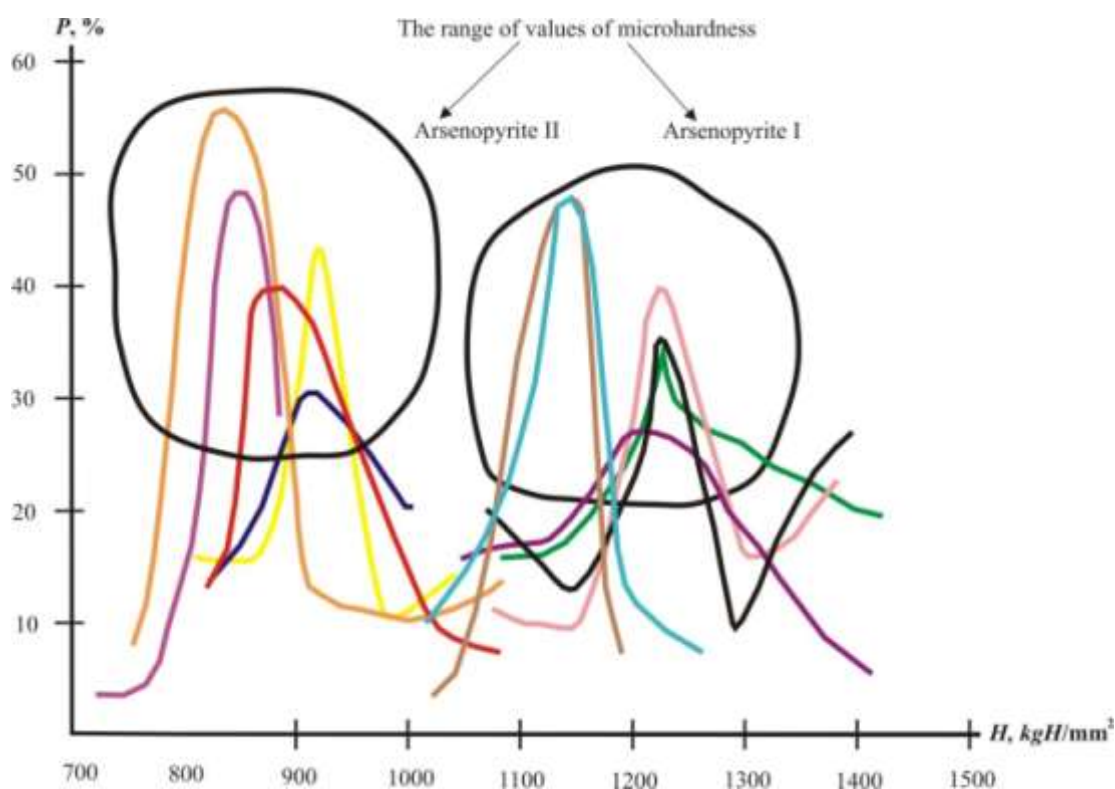**Figure 1**. The spectral reflectance curves of pyrites in Chertovo Koryto deposit.

Figure 2. The spectral reflectance curves of arsenopyrites in Chertovo Koryto deposit.

The research showed that arsenopyrite in terrigenous rocks as porphyroblasts, has a higher microhardness, changing in the interval 1070 1270...kgH/mm^2 with the mean value of 1200 kgH/mm^2. Arsenopyrite, occurring in thin quartz veins and veinlets, is characterized by a lower value ranging from 800...1000 kgf/mm^2, with a mean value of 950 kg/mm^2. The graph of the variational curves is presented in Figure 3. During the study of trace elements in arsenopyrites, it was established that the average content of Co, Ni, and Pb in different generations is approximately the same, in contrast to the content of the noble elements (in arsenopyrite II - increased content of Ag and Au) (Table 2).

Table 2. Average content elements in arsenopyrites.

Element	Arsenopyrites I	Arsenopyrites II	Type of analysis
Co, g/t	400	500	Microprobe
Ni, g/t	800	700	
Pb, g/t	1500	1300	Atomic emission
Au, g/t	17	30	Atomic absorption
Ag, g/t	3	7	

Figure 3.Variational curves of arsenopyrite microhardness (R   shares of occurrence, H - value of microhardness, colors denote different samples).

4. Summary and conclusion
From the above mentioned studies it follows that both mechanical and isomorphic impurities contained in the mineral can influence the reflectivity. Many scientists have come to similar conclusions in the study of physical properties of minerals [2, 3]. Reflectivity can be a good diagnostic parameter, but it is limited by many factors (polishing, clean grains, isomorphic impurities etc.).

The study of microhardness showed that pyrite and arsenopyrite of different generations have different values of microhardness, due to the presence of isomorphic and mechanical impurities and the conditions of formation of minerals as well. In particular, Co and Ni as isomorphic impurities was found in pyrite. These isomorphic impurities decrease the value of microhardness. The presence of e-

type conductivity in pyrite III suggests that Co and Ni are included in the crystal lattice of the mineral. This was confirmed by the decrease of the value of microhardness of up to 1450 kgH/mm^2, because the isomorphic inclusion of Co and Ni reduces the hardness due to the weakening of the bonds in the mineral structure to the higher electropositivity of nickel and cobalt in comparison with iron [12].

It is presupposed that the change of microhardness of arsenopyrite was due to the high Au content and intense tectonic conditions of the formation.

References
[1]   Shumskaja N I and Ljahnickaja V D 1993 *Mineragarficheskie issledovanija rud s primeneniem mikroskopov-spektrofotometrov* Metodicheskoe rukovodstvo (Izd-vo VSEGEI)
[2]   Belozerceva N V, Silichev M K and Avvakumov S V 1998 Vzaimosvjaz' fizicheskih svojstv i sostava arsenopiritov zolotorudnyh mestorozhdenij v terrigennyh otlozhenijah *Mineral'nye aspekty metallogenii Jakutii: Mater. dokl. Sessii* (Jakutsk)
[3]   Mozgova N N 1966 Ob otrazhatel'noj sposobnosti, mikrotverdosti i termoJeDS galenita v svjazi s izomorfnymi primesjami serebra i vismuta *Geologija rudnyh mestorozhdenij* 3
[4]   Nakhla F M 1956 The hardness of metallic minerals in polished section *Econ. Geol*. **51** 8
[5]   Desbarats A J, Parsons M B, Percival J B, Beauchemin S, John Kwong Y T 2011 Geochemistry of mine waters draining a low-sulfide, gold-quartz vein deposit, Bralorne, British Columbia *Applied Geochemistry* **26** 12
[6]   Kucherenko I and Zhang Yuxuan 2014 Metallogenic problems of hydrothermal gold deposit formation: facts and arguments *Scientific and Technical Challenges in the Well Drilling Progress* (24–27 November, Tomsk Polytechnic University, Tomsk) **24**
[7]   Gavrilov R Ju, Khmelev M V and Abramova R N 2014 Volumetric geochemical model of Chortovo Koryto gold-ore deposit (Patom range) *XVIII International Scientific Symposium in Honour of Academician M.A. Usov. Problems of Geology and Subsurface Development* (7–11 April, Tomsk) **21**
[8]   Lebedeva S I 1977 *Mikrotverdost' mineralov* pod red. S A Jushko (M.: Nedra)
[9]   Vagina E A and Rudmin M A 2010 Kristallomorfologija i termojelektricheskie svojstva pirita i arsenopirita v zolotorudnom mestorozhdenii Chertovo koryto (Patomskoe nagor'e) *Izvestija Tomskogo politehnicheskogo universiteta* **1**
[10]   Ding Y C, Xiang A P, He X J and Hu H F 2011 Structural, elastic constants, hardness, and optical properties of pyrite-type dinitrides (CN$_2$, SiN$_2$, GeN$_2$) *Physica B: Condensed Matter* **406** 8
[11]   *Opredelitel' glavnejshih mineralov rud v otrazhennom svete* 1978 (M.: Nedra)
[12]   Korobejnikov A F, Narseev V A, Pshenichkin A Ja and Revjakin P S 1993 *Pirity zolotorudnyh mestorozhdenij (svojstva, zonal'nost', prakticheskoe primenenie)* (M.: TsNIGRI)