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Mineralogical-Geochemical Peculiarities of Ores in Pyritaceous Fields of Filizchai Type in the Greater Caucasus

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Abstract. Pyritaceous fields of the south slope of the Greater Caucasus confined to the Lower-Middle Jurassic sandy clayey deposits are: polygenic polychrone formations which were formed by a complex of hydrothermal sedimentary, hydrothermal metasomatic and hydrothermal metamorphogenic processes of ore formation. Filizchai pyritaceous polymetallic field is the largest in the region and can be characterized by diversity of texture-mineralogical types of ores, rich mineral composition and with geochemical spectrum. Some of the admixture components (Cd, In, Tl, Ga, Ge, Se, Hg) are only in isomorphic forms in ores, others (Te, Bi, Au, Ag, Co, Sn, As) along with it characterize in their own minerals. The Co is mainly concentrated in pyrite, pyrrhotine; Ag, Bi and also Te – in galenite and chalcopyrite; Se – in pyrite, pyrrhotine and galenite; in sphalerite (mainly in marmatite) and chalcopyrite; Cd, Ga, Ge – in sphalerite, mainly in cleiophane; Au – in pyrite and chalcopyrite; Tl – in galenite and colloform pyrite. In all sulphides selenium prevails over tellurium (excepting the late chalcopyrite) and cobalt over nickel. Maximum amount of cobalt is confined to pyrite from pyritaceous polymetallic ores and late generation of pyrrhotine. The nature of the connection between chemical elements in ores coordinates with determined stages of minerals formation. The main productive stage of ore formation bringing the main mass of gold, silver, rare and other precious components of ores are sulphosalt polymetallic stage of sulphur ploymetallic stage. Comparative analysis of absolute content of gold, silver and values of gold-silver relation in pyrite fields ores of region with appropriate values in meteorite standard indirectly indicates the relationship between gold-silver mineralization and assimilation crust source.

Introduction

Heterogeneous pyritaceous polymetallic and copper-zinc pyrrhotite deposits in the south slope of the Greater Caucasus located in the Lower-Middle Jurassic terrigenous sediments, which were formed in terms of a wide variation of physio-chemical parameters of mineral formation, are characterized by specific mineralogical geochemical peculiarities. Ores in the investigated pyritaceous deposits of a Filizchai type combine features of Ural, Cyprus, Kuroko and Bessi types. Their common features with the first two types are a high amount of iron and increased concentrations of some siderophile elements (Co, Ni, Mn) in pyrite, and with ores of a Kuroko type proximity of correlation of main components (Zn, Pb, Cu) and amounts of chalcophile admixturing components (Sb, As, Bi, Sn) in pyrite and in ores on the whole by high concentration in the latter of sulfosalts of Ag, Pb, Cu and Bi. Their common features with ores of a Bessi type is similarity of main minerals and levels of concentrations of noble metals (Au, Ag) in ores.

Mineral Content of Ores and Peculiarities of Ore-Formation

The Filizchai field is the largest pyritaceous polymetallic field in the Caucasus. Its stratum like ore deposits is the most complex due to total combination of different natural types of ores. Texture mineralogical types of ores as a part of united deposits occupy regular position: the most widespread bedded foliated pyritaceous polymetallic ores (more than 70 % of the deposit volume) are located mainly in the hanging wall. Massive pyritaceous polymetallic and sulfur pyritaceous ores occur together with bedded foliated ones mainly in deep horizons in the north east of the field. Spotted breccia-like sulfur pyritaceous and pyritaceous polymetallic ores and copper pyrrhotine ores of a massive composition occur exclusively in the upper horizons in the east of the field from the bottom side of the deposits bottom. They are replaced by vein impregnated ores both down the dip and along strike.

Structure of top and base of one bed-like field deposit differentiates by some peculiarities. So, top of the deposit is more stable on all its extension. Base of the deposit is characterized by complex structure including sharp contacts with ore enclosing rocks. On the other hand, a great variety of natural ore types is confined to the base. Intensive hydrothermal metasomatic rocks change (carbonatization, selicification, chloritization, sericitization) can be found in subore series.

Ores in the Filizchai field possesses rich mineral composition. Pyrite is dominant sulfide mineral. Sphalerite, galenite, chalcopyrite and pyrrhotine are also present. The secondary and rare minerals are marcasite, arsenopyrite, cobaltine, linnaeite, magnetite, tennantite, tetrahedrite; different sulfosalts of copper and lead; bismuth minerals, tellurides of gold and silver. Hypergene

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minerals are iron hydroxides, malachite, azurite, chalcocite, covellite, tenorite, chalkantite, cerussite, anglesite, jarosite and goslarite. Non ore minerals are represented by quartz, carbonates, chlorite, sericite etc.

Ore-formation occurred by three stages in studied fields. On the first stage massive hydrothermal sedimentary sulphurous pyrite ores were bedded. The formation of the second stage of hydrothermal metasomatic pyrite polymetallic ores was the intrusion of constant differentiated dikes. On the third stage hydrothermal metamorphogenic copper-pyrrhotine ores were formed. Ore deposition occurred under temperature 150°C on the first stage (Gurbanov, et. al, 1983). Study of temperature in pyrite fields, ores formation by homogeneity of gas fluid intrusion method. Tvalchrelidze (1987) provided the following results; pyrite polymetallic ores in average 120°C (Filizchai field) and 145°C (Katsdag field), copper-pyrrhotine – on average 300°C. The same temperature for copper-pyrrhotine ores was defined by us through pyrite-pyrrhotine geothermometer. On the basis of isotopic thermometry of the basic ore forming sulphides. Zairi et.al. (1980) defined the temperature of sulphide ores crystallization in Katekh, Filizchai and Katsdag fields. It has been determined the later copper-pyrrhotine stage of mineral formation can be characterized by high temperature (by average 440°C in Filizchai and 410°C in Katsdag) in comparison with earlier pyrite-polymetallic stage (pyrite stage on average 310°C and polymetallic on average 240°C). Using the data dealing with elements admixture content (Fe, In, Co, Sb, Ga, Tl) in sphalerite and galenite, criterion of formation, conditional index of temperature was calculated for pyrite polymetallic ores of Filizchai field. The obtained temperature index 218-235°C perfectly coordinates with above mentioned results of other investigators.

As a result of many research works, it was defined the indices of trace elements concentrations and values of their relations can be reliable indicators of physico-chemical conditions of ore-formation environment. It is generally known due to specific nature of its geochemical properties, rare elements are more sensitive to the change of physico-chemical conditions of ore-formation than the basic components. The behaviour of trace elements in ores depends much on both acid alkaline solution and on temperature of mineral formation environment and also on redox condition. Acid alkaline properties of the solutions and nature of their change is the most important physico-chemical factor of geochemical migration of the components. Thus, the ores of the copper pyrite polymetallic fields of the South Slope of the Greater Caucasus are characterized by a wide geochemical spectrum. In studied fields ore formation occurred under changing solution acid alkalinity conditions. Pyrite polymetallic ores were formed from more alkaline solutions than copper pyrrhotine ores of the following stage. Emanation of sulphosalts antimony kinds of grey ores (tetrahedrite) in productive polymetallic rare metal association of pyrite polymetallic stage of ore formation in Filizchai field shows alkaline nature of solution. Accumulation of cadmium, indium, thallium, bismuth in ores of studied fields occurred in more alkaline environment. Redox conditions play a definite role in the concentration process and dispersion of rare elements. According to Tischendorf (1966) redox system potential influences greatly on selenium distribution between sulphides. As a whole, formation of studied pyrite polymetallic and copper pyrrhotine ores occurred by variable value of redox regime.

Results and Discussion

It is known that ores of pyritaceous deposits are a very important source of some rare and noble metals. The investigated pyritaceous deposits in the South slope of the Greater Caucasus are characterized by a wide range of admixturing components. Together with common features in the distribution of main and attendant components, in texture mineralogical types of ores and main sulfide minerals one can notice certain specific features for every deposit. For the majority of elements admixtures despite some difference between minerals carriers, the concentrations in all the studied deposits are almost one and the same sulfide minerals. Among the rare elements of a special attention is a group of elements with a common disperse character of distribution and nearly complete absence of even slightest commercial accumulations with a tendency of accumulation in endogenic ore deposits. In geochemical literature these components (Cd, In, Tl, Ga, Ge, Bi, Se, Te, Re) compose a group of chalkophile rare elements. In many countries attendant extraction of the above mentioned components out of sulfide ores have been traditionally conducted for decades.

Cadmium: It is constant admixture of sphalerite (maximum, up to 0.5 %) of the investigated ores. Its concentration grows during mineral formation from marmatite to cleiophane. In other sulfides its amount is 10^2 lower. Increased concentrations of indium are linked with sulfides possessing the quadruple coordination (sphalerite, chalcopyrite) and for minerals with the sextuple coordination (pyrite, pyrrhotine, galenite) low concentrations of the element are typical. In the dark-coloured varieties of sphalerite amount of indium is nearly two times higher than in the light coloured (0.0095 % and 0.0055 % respective). Existence of two varieties of the mineral is indicated by a bimodal character of histogram of frequency of indium distribution in sphaleirite from Filizchai and Katsdag fields. Our investigations also demonstrated absence of a clear linkage between the change of amount of indium in sphalerite and amount of iron in it in the pyritaceous deposits in the region. In the investigated ores tallium tends to accumulate, on the one hand, in lead minerals (galenite and burnonite) and on the other hand, in collomorph pyrite. In the lead sulfide tallium exists isomorphically according to the scheme: $2\,Pb^{2+} \rightarrow Tl^{1+} + Sb^{3+}(Bi^{3+})$, and in pyrite as a sorbtion. Pyrite of endogenous origin contains tallium ten times higher than of sedimentary origin. Maximum amount of the element was determined in massive thin grained pyrite polymetallic ore in the Katekh field 0.056 % (Novruzov, 2003).

Gallium: It is not typical admixture of the investigated. ores. Its amount is different in vein impregnated ores (on average 0.0019 %). This is due to gallium content of the ore enclosing sandy clayey deposits as a result of accumulation of the element in the silicate component. The highest amount of the element (up to 0.004 %) was determined in the light spahlerite. Amount of germanium is low. Decreased background of germanium content of these pyritaceous deposits is probably linked with the initial impoverishment of the ore forming solutions by this element. It is quite obvious that the silicate condition played an important role in the distribution of the element as well, a small amount of which was dispersed in the enclosing deposits due to crystal chemical proximity of Ge^{4+} and Si^{4+}.

Selenium and Tellurium: There are among the admixturing components of ores occurring everywhere. Galenite together with pyrite and pyrrhotine are minerals-concentrators of selenium. A certain role is played by chalcopyrite. In the region the Katekh pyritaceous-polymetallic field is famous for selenium content of galenites. The highest amount of the element is up to 0.036 % there (on average 0.019 %). Concentration of tellurium in the mineral (on average 0.009 %) is of a certain importance. Unlike selenium, besides isomorphic existence in sulfides, it is individualized in numerous proper minerals. Among copper-pyrrhotine mineral association of pyritaceous deposits in the region, chalcopyrite is the only leading sulfide mineral where tellurium prevails over selenium. In the distribution of selenium in varieties of pyrite there was determined relation of increased concentrations of the element to the crystal variety of the mineral. Thus, there exists dependence between the amount of selenium and crystal maturity of pyrite.

Bismuth: It is a constant companion of the investigated ores. Its mineral concentrator is galenite (see Table). Due to the highest amount of galenite and also wide spreading of bismuth minerals (bismuthite, tellurobismuthite, tetradymite, emplectite, claprotolite, beegerite, cosalite etc.) in the bedded foliated and massive pyritaceous polymetallic ores in the Filizchai field, exactly these texture mineralogical types of ore are the most bismuth bearing.

Gold and Silver: These are typemorphic admixtures of pyritaceous ores in the region. Main amounts of both elements is linked with productive pyritaceous-polymetallic ore formation. Maximum concentration of gold in some samples of pyritaceous polymetallic ores is 3.6×10^{-4} %, silver 3.8×10^{-2} %. Pyrite and chalcopyrite are minerals-concentrators of gold, and galenite of silver.

A certain role is played by secondary (according to their spread) minerals i.e. arsenopyrite and tetraedrite.

Table 1. Average amount of rare and noble metals in main sulfide minerals in copper pyritaceous polymetallic deposits in the South slope of the Greater Caucasus (10^{-4}%)

Elements	Pyrite	Sphalerite	Galenite	Chalcopyrite	Pyrrhotine
Cd	26	1700	30	18	17
In	3,6	49,5	6,8	22	2,1
Tl	13,6	9,4	19	3,1	1,5
Ga	3	13,5	2,9	2,6	2,1
Ge	1,7	2,4	0,5	1,3	1
Se	25	13,2	115	10,7	43,5
Te	3,9	8,7	50	20	5
Bi	43,5	30	340	87	50
Au	0,62	0,36	0,04	0,7	0,28
Ag	32	48	620	100	20

Usually they contain highest concentrations accordingly of gold and silver. This is evidenced by significant correlations in pairs of elements Au-As and Ag-Sb in ores. Existence of proper minerals of noble metals in the investigated ores is of importance as well (petcite, hessite, nagiagite, argentite, freibergite, discrasite, benzhamenite, volynskite, native gold and silver). Values of silver-gold relation grow in the Filizchai type as related to the cyprusian, ural, kuroko and bessi types of pyritaceous deposits (Hutchinson, 1973; Eremin and Dergachov, 2000).

In the commercial technological types and sorts of ores from the Filizchai field values of relation of average amount of silver to gold regularity decrease as follows: initial mixed oxidated ores. Concentrations of these elements and also their relative amounts (Au/ Cu, Zn, Pb and Ag/Cu, Zn, Pb) distinctly grow in the same direction. Limits of gold and silver amounts in the mixed ores are (1×10^{-4} %): 0.4-3.5 and 26.5-162 and in the oxidated they are 1-13 and 12-773 respectively. These ores in the field are not widely spread. They are 2.2 % and 0.5 % of the total volume of the balance ores.

The cobalt presence of these ores is of a great importance. In Filizchai field this element contains by equal amount, on average $2.3\text{-}10^{-2}$ % in bedded foliated and massive pyrite polymetallic ores. In massive sulphurous pyrite ores cobalt amount increases by two times ($4.6\text{-}10^{-2}$ %). In copper pyrrhotine ores cobalt concentration is a bit lesser than in sulphurous pyrite ones. A systematic cobalt increase can be found from earlier to late generations of hexane pyrrhotine. Maximum element concentration is confined to pyrite III, which contains the basic part of pyrite pollymetallic ores.

The nature of relationship between chemical elements in multicomponent ores of Filizchai field corresponds to established stages of mineral formation. The main productive stage of ore formation bringing the basic mass of noble metals (Au, Ag) rare and other valuable components of ore is sulphosalt polymetallic stage of pyrite polymetallic stage. Relations between components in ores of studied field as a whole can be characterized by complex form and various close set and this is caused by heterogeneity of complex ores deposits formation in

Filizchai pyrite polymetallic field. It is noteworthy as a result of multistage process of ore formation and supervision of one mineral associations over other ones the connections between components are not always vivid. As a whole, the use of correlation analysis methods for qualitative assessment of dependence between chemical elements in some types of Filizchai field ores allows to define genetic connections of ore components with definite mineral associations. So, on the basis of correlation analysis one can assume that gold and silver associate with chalchophile elements group in pyrite polymetallic and partially in sulphurous-pyrite ores and they are closely connected with antimony and arsenic mineralization (Novruzov, 2006).

Mineralogical-geochemical Zonation: As a result of investigations of spatial distribution, there were determined different types of mineralogical-geochemical zoning in the ore deposits. In the South slope of the Greater Caucasus as passing from north-west to south-east, regional zoning is recorded. It is expressed in the change of copper pyrrhotine ores by pyritaceous polymetallic. In the same direction there also occurs decrease of concentration of copper and increase of amount of lead. Change of mineral composition is also reflected in the character of distribution of concentrations of admixturing components. At the same time in every field there were determined mineralogical geochemical zonings along strike, dip and thickness of ore deposits. Common regularity for pyritaceous fields in the region is the decrease of concentrations of zink, lead, gold, silver, bithmuth, cadmium, gallum, germanium, antimony, mercury and rarely, arsenic, manganese and thallium from the upper horizons towards the lower ones, whereas copper, cobalt and selenium from the lower horizons towards the upper ones. Zonation on ore deposit fall can be found in distribution of trace elements in pyrite, pyrrhotine, chalcopyrite and in sphalerite. In pyrite the content of silver, thallium and germanium reduces and indium, gold, selenium and tellurium increases on deposit extension from the western flank to eastern. Cadmium and bismuth are more concentrated in the central part of deposits. The growth of indium concentration and reduction of thallium, gold and silver can be found in this direction in sphalerite.

Maximums of average weighted amounts of lead and zink have much in common and occupy nearly the whole west part of Filizchai deposit starting from the central profile. Increased concentrations of copper form local areas in the east flank and also in the central part of the deposit. Areas of the highest enrichment by zinc and copper as well as by lead and copper are separated: maximums of one element concentration coincide with minimums of another. Zoning in the distribution of amounts of some elements admixtures (Au, Ag, Cd, Tl, Ge, Se, Co) by thickness of ore deposits manifests itself distinctly in main sulfide minerals, especially in pyrite and chalcopyrite (Novruzov and Agayev, 1983, 1985). So, from lying flank of deposit towards a hanging one the content of gold, silver, cadmium, indium, thallium, germanium and bismuth increases in pyrite and spahlerite. Here the content of cobalt, selenium and tellurium is more in lying flank of deposit. The same situation can be defined in chalcopyrite excepting selenium.

Sources of Ore: Many research consider the metals and sulphur are mainly of juvenile origin in pyrite fields of the South slope of the Greater Caucasus. According to Tvalchrelidze (1987) juvenile and assimilation sources of the matter prevail nearly in all types of pyrite fields.

As a result of research we made an attempt to clarify the source of ore matter using data of gold presence and silver presence in ores. The distribution of average contents of noble metals (Au and Ag) calculated for conventional 100 % sulphide and standardizing on coaly chondrite C1 according to existing method (Naldrett, 1984) allows to define some patterns. As it is seen on figure absolute contents of gold by one order, silver and Ag/Au value by 2-3 orders and more exceed their appropriate values in meteorite standard. Determined peculiarities are indirect reflection of gold-silver mineralization connection in studied ores with assimilation crust source just the same to orealtai pyrite-polymetallic fields determined by Lapukhov and Ivanov (1993).

Conclusion

Comparative analysis of geochemical peculiarities of hydrothermal metasomatic field ores allows to define some specific peculiarities of trace elements distribution. According to many researches' data hydrothermal sedimentary ores of pyrite polymetallic fields on general low level of contents and rather restricted set of trace elements they perfectly differ from hydrothermal metasomatic formations which are close to them by their mineral composition. As a whole the content of trace elements and values of their indicator relations (Se/Te, Ag/Au) are the important geochemical indicators of sulphide minerals formation conditions.

Parameters of distribution of rare and noble metals in different texture mineralogical types of ores and main sulfide minerals of pyritaceous deposits in the region determined by us, being additional indices of physico-chemical terms of mineral formation, are related to type morphic features of stratiform pyritaceous polymetallic deposits of hydrothermal metasomatic type in the South slope of the Greater Caucasus.

And finally, it should be mentioned that very high concentrations of the most elements admixtures in Filizchai, as compared with other fields in the region, are linked first of all, with bedded foliated and massive pyritaceous polymetallic types of ores. They play dominant role in the deposit's composition where products of sulfosaline polymetallic mineral association are rather widespread. Relation of maximum concentrations of rare and noble metals as well as Co, Sn, As, Sb, Hg etc. to the most important commercial pyritaceous polymetallic ores much more exceeds complex value of the latter.

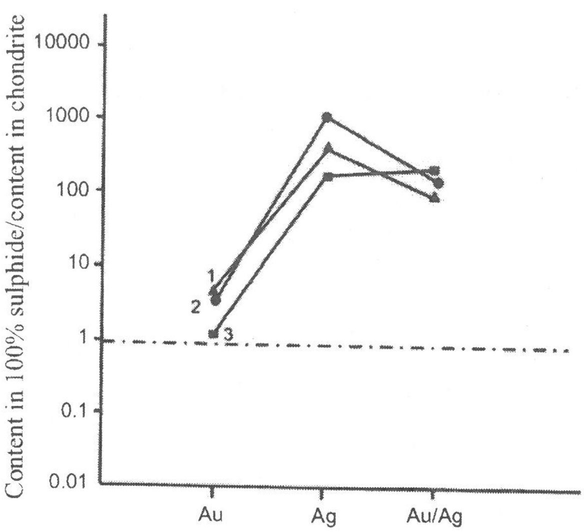

Fig. 1. Distribution of average contents of Au and Ag in the main ores types on basis of conventional 100% sulphide standardizing on coaly chondrite C1. Fields: 1 – Filizchai, 2 – Katekh, 3 – Kasdag.

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