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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

GEOCHEMICAL MODEL AND PREDICTION-INVESTIGATION CRITERIA OF MINERALIZATION OF BLACK SHALES OF THE DURUJA ZONE OF THE SOUTHERN SLOPE OF THE GREATER CAUCASUS

Speciality: 2503.01 – Geochemistry, geochemical prospecting methods of minerals

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THE GENERAL CHARACTERISTICS OF THE WORK

Relevance and the degree of scientific development of the topic. Researching the accumulation potential of noble, non-ferrous, radioactive metals, as well as rare and rare earth elements of black shales, which are characterized by a wide range of chemical elements, plays an important role in discovering their new, unconventional resources.

Localized deposits with rich resources of the abovementioned elements have been found in black shales in several regions of the world. From this point of view, the Duruja structure-formation zone, where the Middle Jurassic rocks of the black shale formation of the southern slope of the Greater Caucasus are widely distributed and high concentrations of gold, molybdenum and a number of other metals have been observed as a result of the prospecting work, attracts special attention.

It is of particular importance to investigate the occurrence of mixed elements of ore and nonmetallic minerals of the research area, to study the conditions of ore formation, to determine the factors affecting ore accumulation, to investigate ore sources based on the analysis of sulfur isotopic composition in sulfides of the zone, to reveal the anomalous areas of the main components in the rocks.

Research object and subject. The Duruja structure-formation zone, which is the object of the research, is separated from the Zagatala-Govdag zone in the north by the Gaynar fault, and from the Vandam zone by the Zangi fault in the south. The rocks located between numerous transverse faults of different sizes and separate branches of the faults have been intensively dislocated, subjected to strong dynamometamorphism and schistosity, hydrothermal alterations such as graphitization, chloritization and limonitization.

Concretions occupying a certain stratigraphic position in the section of the clay layer of the zone and containing sandy-siderite, clayey-siderite, pyrite-siderite and mainly pyrite, and rock layers containing numerous such concretions play an important role. Researches were carried out in mineralization areas – Lekit-Gum, Gizilgaya, Aglig-Filfilli and Galajik, which are more interesting in terms of prospects for the search for noble, non-ferrous, radioactive

metals, as well as rare and rare earth elements and consist of sediments of aspid and terrigenous-flyschoid formations of Lower and Upper Aalenian age of the Middle Jurassic.

Research aims and objectives. The research aim is to study the distribution, accumulation characteristics and occurrence forms of noble, non-ferrous metals, rare, radioactive and rare earth elements in the black shales of the Duruja structural-formation zone, and to develop the criteria for the prediction and investigation of blind ore body.

The main objectives of the research work are the following:

1. Study of the material composition of the terrigenous-sedimentary complex of the Duruja zone;
2. Study of textural-structural characteristics and mineral composition of ores;
3. Study of the geochemical properties of ores and rocks of the region;
4. Investigation of occurrences of mixed elements in ore- and rock-forming minerals;
5. Revealing factors affecting ore accumulation in the region;
6. Investigation of the source of the ore matter;
7. Compilation of mathematical-statistical and geochemical models reflecting the distribution of noble, non-ferrous metals, rare, radioactive and rare earth elements in the black shales of the Duruja zone;
8. Separation of geochemical anomalous areas in the research area and development of efficient geochemical-mineralogical prediction-search criteria of blind ore body.

Research methods. The results of analyzes of more than 1200 ore, mineral and rock samples taken by the author were processed in the dissertation work. Ore and rock samples were analyzed by various methods such as X-ray-fluorescence, emission spectral, mass-spectrometric, atomic-absorption, IR-spectrometric. “Perkin Elmer” atomic absorption spectrometer was used for re-determination of gold, silver, copper and zinc in samples, and X-ray-fluorescence mass spectrometer of Agilent Company was used for determination of other elements.

While analyzing petrochemical data, various petrochemical modules, indicators to study sedimentary rocks, diagrams by P.B.Rosen, R.J.Korsh, M.P.Bakhtin, S.Maynard were used to investigate the sources

and origins of rock materials brought to the sedimentation basin. The petrographic properties of rocks and mineralogical properties of ores were studied using "Carl Zeiss", "MIN-9" and "MIN-8" microscopes in transmitted and reflected rays on 250 thin sections and 200 polished sections.

More than 50 monomineral samples were extracted from ore and rocks under the MBS-1 binocular microscope, and the analysis of their elemental mixtures was carried out using the X-ray-fluorescence method in the "PICOFOX" analyzer.

The surface dimensions of 140 monomineral grains of ore and non-metallic minerals in thin sections and polished sections were determined by "SEM" electron microscope, and their morphological characteristics were studied. Precise diagnosis of minerals in 130 samples was carried out based on the results of their X-ray diffractometric analysis.

The amount of organic matter in 60 samples was studied by thermolysis and pyrolysis, and the element composition of the organic matter extracted from 30 samples was determined in the ICP-MS (NexION 300D) mass spectrometer inductively coupled with argon plasma with high sensitivity. The size of the nanoparticles of 30 samples was determined in the "HORIBA SZ-100" device, and the samples that are sorted according to their size were again analyzed in a mass spectrometer. Isotope analysis of sulfur in sulfides was performed by the local laser method at the Caucasian Institute of Mineral Raw Materials (Georgia).

Mathematical-statistical analysis and modeling of the obtained analytical data was carried out using "Statgraph-18", "Statistica-10" computer programs. The distribution models of the elements characterized by high concentrations obtained as a result of the researches have been drawn up on mineralization areas using the "Arc GIS" computer program, and geochemical anomalous zones have been separated.

The main points of the defense:

1. Formation of sulphide ores characterized by richness of textural-structural types in Duruja structure-formation zone associated with syngenetic and epigenetic processes in two stages of mineralization;

2. The important role of mineralogical features of the region's terrigenous-sedimentary complex, the high amount of organic matter

in the rocks, all Caucasian and transversal faults in ore formation;

3. Models reflecting the distribution and accumulation of chemical elements in mineralization areas, anomalous areas allocated for the search of noble, non-ferrous, radioactive metals, rare and rare earth elements based on these models, and geochemical-mineralogical prediction-search criteria of blind ore body.

Scientific novelty of the research:

1. For the first time, the distribution of rare and rare earth elements in the rocks of the Duruja structural-formation zone was studied, and the occurrence forms of mixed elements in ore and non-ore minerals were observed.

2. Mineralogical-geochemical zoning from the northwest to the southeast was revealed according to the characteristics of the distribution of mineral-concentrators and mixed elements found in the research area.

3. In order to investigate the source of the ore matter, the isotope analysis of sulfur in the sulphides was carried out for the first time, and the biogenic and mantle origin of the mineralization was determined.

4. Anomalous zones of noble, rare, rare earth, and radioactive elements were separated in the Duruja structural-formation, their geochemical, mathematical-statistical models were drawn up, the prediction-search criteria of blind ore body were developed, and prospective areas for the search and exploration of the abovementioned elements were proposed.

Theoretical and practical significance of research. The study of mineralogical-geochemical properties of sulphide ores located in the black shales of the Duruja zone and the rocks of the black shale layer where they are localized, determining the factors affecting ore accumulation, and investigating the sources of ore matter are of great scientific importance.

Revealing promising areas for the search of noble, non-ferrous, radioactive metals, as well as rare and rare earth elements, discovery of blind ore body and presentation of prediction-investigation criteria are of great practical importance.

Approbation and use. The results of the dissertation work were presented at the 9th International scientific-practical conference

(Russia, Kazan, 2014), the 3rd All-Russian scientific conference (Blagoveshensk, 2014), the 8th International conference (Maykop, Russia, 2016), the seminar of Young Scientists (ANAS Institute of Geology and Geophysics, Baku, 2018), the 7th International conference of young scientists and students (Baku, 2018), the Republican conference "Geology: problems, prospects" dedicated to the 99th anniversary of the birth of the National Leader Heydar Aliyev (Baku, 2022). 7 articles (1 article in journals on Web of Science database, 1 article on GeoRef database) and 5 theses were published in foreign and local journals on the subject.

Name of the institution where the dissertation work was performed. The dissertation work was performed at the Institute of Geology and Geophysics of the Ministry of Science and Education of the Republic of Azerbaijan.

The total volume of the dissertation with a character by noting the volume of the structural sections of the dissertation separately. The dissertation consists of 185 pages, including introduction, 6 chapters, conclusions and suggestions, a list of references containing 115 titles, 80 figures, 22 tables. The total volume of the dissertation is 180120 characters, including the introductory part – 12980, Chapter I – 9125, Chapter II – 14400, Chapter III – 12700, Chapter IV – 33670, Chapter V – 64355, Chapter VI – 30584, Conclusion – 2306.

The author expresses her gratitude to his late supervisor Ch.M.Kashkay, Doctor of Geology and Mineralogy, and second supervisor R.B.Karimov, Candidate of Geology and Mineralogy, who gave valuable advice in the process of completing the dissertation, to Academician Ak.A.Alizadeh, Executive Director, Corresponding Member of ANAS D.A.Huseynov for the conditions they created for conducting field studies, relevant analyzes and preparing the dissertation, to Candidate of Geology and Mineralogy S.F.Valizadeh for her advice during the microscopic studies, and to A.N.Agayev, M.I.Abdullayev, N.M.Sadigov, N.F.Naghiyev, S.G.Martynova, A.J.Ibadzadeh, A.S.Amirov, S.A.Zeynalova, who supported in conducting analytical work, to Correspondent Member of ANAS G.I.Jalalov for his recommendations in the statistical analysis of analytical data.

THE MAIN CONTENT OF THE RESEARCH

CHAPTER I. THE CURRENT STATE OF GEOLOGICAL STUDY OF THE DURUJA ZONE OF THE SOUTHERN SLOPE OF THE GREATER CAUCASUS

Initial data (in the period up to 1917) related to the geology of the Azerbaijani part of the southeastern slope of the Greater Caucasus was obtained as a result of research by V.H.Abikh, K.I.Bogdanovich, S.Simonovich, later (1917-1956 years) by K.N.Paffenholz, D.V.Drobyshev, V.V.Weber, A.N.Solovkin, A.Ch.Sultanov, M.M.Aliyev, V.Y.Khain.

The discovery of several pyrite-polymetallic deposits and occurrences on the southern slope of the Greater Caucasus in the late 1950s and early 1960s aroused considerable interest in conducting geological works related to the search and exploration of non-ferrous metals in this region.

In 1956-1984, A.Sh.Shikhalibeyli, Z.I.Isayev, M.P.Yolchuyev, H.A.Aliyev, I.Sh.Mammadov, A.Kh.Baloglanov, Ya.F.Podgorny conducted investigation and mapping works on the southern slope of the Greater Caucasus, allocated promising ore-bearing areas such as Kungut, Dashagıl, Agchay, Galajik, etc. During the prospecting work, it was noted that the black shales of the Duruja zone are suitable for the accumulation of precious metals, and 1:100,000 scale geological map was created based on the obtained data on the stratigraphy, tectonics and magmatism of the abovementioned region. A.Sh.Shikhalibeyli, who noted that the Duruja zone had a complex tectonic structure, justified the mentioned region as a structural unit that could be promising in terms of ore accumulation.

In 1961-1967, Ye.D.Yakovenko, A.A.Nabiyev, M.A.Akhundov, V.V.Alekseyev, H.M.Ahmedov, M.M.Rajabov, V.N.Nagiyev and others carried out geophysical investigations and aeromagnetic surveys in various ways on the southern slope of the Greater Caucasus, and suggested the presence of positive anomalies in Gabala and Gamarvan areas. J.J.Mazanov (1969) studied the clay shales of the southern slope of the Great Caucasus with different methods (optical, thermal, radiographic), and distinguished their mica, phyllite and phyllite-like, aspid and spotted rock types.

As a result of exploration work conducted by A.H.Baloglanov and Ya.F.Podgorny in the Duruja zone in 1975, several similar char-

acteristics of the rocks of the Duruja zone and the ore-hosting rocks of the Saribash zone were discovered, and it was observed that this zone is also promising for the search for pyrite mineralization.

A.Kh.Baloglanov, A.I.Mammadov and others continued the investigations in the research area. Works on geophysical well logging were carried out by D.A.Abdullayev, surface geophysical works by H.A.Ahmadov, and logging works by O.A.Nurullayev during this period. As a result of the research work, it was determined that the rocks of the Duruja zone have high concentrations of several elements (Cu, Zn, Fe, Pb, Ag, As, Se, Mo, V, etc.).

Summarizing the results of geological prospecting works by V.B.Agayev, Z.I.Mammadov, M.I.Jafarov, N.R.Ilyasov, N.A.Musayev, M.P.Yolchuyev, H.A.Chelebi and others in order to study the gold prospects of the black shales of the Duruja zone, it was determined that the tectonic fractures and fault zones of the sedimentary rock complex, and the areas where sulphidation is observed are more promising for noble metals.

N.R.Ilyasov (1976-1980), F.M.Abdullayev, M.I.Jafarov (1982-1985) found traces of gold in some of the samples taken from tectonic fault zones, and showed that only quartzization and intense sulphide mineralization are characteristic for gold mineralization, and clay shales are not promising in terms of gold prospecting.

In recent years (2020-2022), a group of researchers (R.B.Karimov, S.F.Valizadeh, T.S.Gadirova and others, 2022) of the ANAS Institute of Geology and Geophysics has studied the characteristics of distribution and accumulation of noble, rare, radioactive metals and rare earth elements in the Alene-aged sediments of the Duruja zone, as well as carried out a geochemical assessment of the accumulation potential of rare earth elements by these rocks.

So, the results of the conducted exploration and scientific-research work show that it is necessary to study the following several issues in the Duruja structure-formation zone: study of occurrences and regularities of distribution of noble, non-ferrous, radioactive metals, rare and rare earth elements in ores and rocks, factors affecting ore accumulation, investigation of ore sources based on the analysis of sulfur isotope composition in sulphides of the Duruja zone, revealing anomalous areas and blind ore body.

CHAPTER II. GEOLOGICAL STRUCTURE OF DURUJA STRUCTURE-FORMATION ZONE

2.1. Geological characteristics of model mineralization areas

The Azerbaijani section of the southern slope of the Great Caucasus is a megaanticlinorium that has undergone a complex geological development period, has been subjected to various tectonic processes, and has a mosaic geological-tectonic structure.[1] The Duruja structural-formation zone, where we conducted the study, is bounded by the Gaynar fault from the north – Zagatala-Govdag synclinorium along the strike direction, and by the Zangi fault from the south – the Vandam anticlinorium.[2] The Lower and Middle Aalenian sediments of aspid, terrigenous-flyschoid formations of the region are observed in the Caucasian oriented area between Lekitchay-Sulutchay at a distance of up to 200 km with a thickness of 0.3-4.5 km.

The aspid formation consists of graphitized black shales, and the terrigenous flyschoid formation consists of rhythmic alternation of polymict sandstones, siltstones, siltstone-sandstones, and shales with lenticular small layers of syngenetic pyrite. Sand-siderite, clay-siderite, pyrite-siderite, and significantly pyrite-containing concretions and concretionary layers, which occupy a certain stratigraphic position in contact with the sediments of the abovementioned formations and form a horizon with a thickness of up to 12 m, continuing quite consistently in the strike direction, also play an important role.

The Gaynar fault is of regional depth origin and is observed continuously throughout the studied Caucasian oriented area. Various amplitude landslides, transverse upthrust, and alterations such as budinage are observed in the intersection zones of the meridional faults with the Gaynar fault, which indicates that intense metamorphism is occurred in the fault zone.

The bedding of Zangi fault, which is located in the south of the region and consists of numerous upthrust and thrust, is fixed, and shale formation, budinage and crushing are observed along the fault.

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[1] Шихалибейли, Э.Ш. Геологическое строение и развитие Азербайджанской части южного склона Большого Кавказа / Э.Ш. Шихалибейли. – Баку: АН Аз.ССР, – 1956. – 228 с.

[2] Геология Азербайджана: [в 7 томах] / Под ред. В.Е.Хаина и Ак.А.Ализаде. – Баку: Nafta-Press, – т. 4. – 2005. – 506 с.

Repeated tectonic movements in the research area have led to massive crushing, deformation, intense shale formation of rocks, as well as the development of metamorphic and metasomatic processes, which created favorable conditions for the formation of ore accumulation in the area (Figure 1).

All discovered ore fields, accumulations and anomalous points are structurally associated with faults. It should be noted that besides primary sedimentation processes, intensively developed volcanism along the northern part of the Vandam zone also played an important role in the formation of their mineral composition.[3]

Figure 1. Examples of observed epigenetic and syngenetic mineralization in the Duruja zone

CHAPTER III. TEXTURAL AND STRUCTURAL CHARACTERISTICS AND MINERAL COMPOSITION OF THE ORES OF DURUJA STRUCTURE-FORMATION ZONE

3.1. Textural and structural characteristics of ores

The sulphide ores of the Duruja zone are characterized by rough, veined, veined-rough, bended, spotted, massive, breccia-like and core-like textures.

[3] Керимов, Р.Б., Самедова, Р.А., Гадирова, Т.С. Петро-геохимические особенности и перспективы рудоносности меловых вулканогенных комплексов Вандамской зоны Южного склона Большого Кавказа // – Рига: Ежемесячный международный научный журнал «SCITECHNOLOGY», – 2018. №10. – с. 7-10

Rough-type ores, which are much more dominant due to the occurrence intensity, are represented by rough sulfide mineral crystals that are distributed unevenly in wallrocks in most cases. Vein-type ores develop in the areas where epigenetic sulfides are distributed, accompanied by quartz and calcite. Locally, the bended texture is occurred as an alternation of sulfide bands and bands of non-metallic minerals. Occurrences in which the alternation of ore and non-metallic bands are not clearly expressed are often observed.

The ores in the areas we researched are characterized by a variety of structural types. Ore minerals are represented by hypidiomorphous, allotriomorphous, concentric-zonal, radial, globular, relict, druse, annular, rimmed, cataclastic and a number of other structural aggregates (Figure 2).

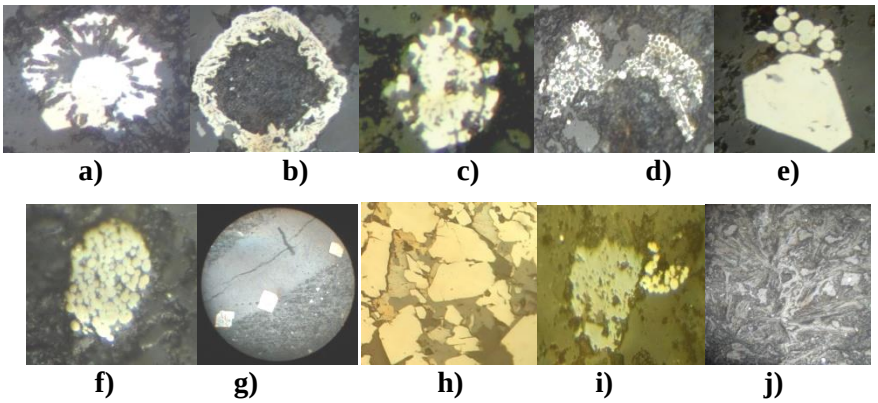

Figure 2. Structures of mineral aggregates. Different aggregate forms of pyrite (white): a) socket. Polished section. X 210; b) lace. Polished section. X 210; c) spherical. Polished section. X 210; d) like beeswax. Polished section. X 210; e) a accumulation of well trimmed coarse grains and pointed grains. Polished section. X 90; f) globular. Polished section. X 210; g) idiomorphous. Polished section. X 90; h) irregularly shaped pyrite-sphalerite-galenite-chalcopyrite joint. Polished section. X 90; i) accumulation of irregularly shaped small grained of pyrite (white) and scale-shaped molybdenite (light gray). Polished section. X 90; j) branch- and thorn-like aggregates of pyrolusite. Polished section. X 90.

3.2. Mineral composition of ores

The most widespread mineral of the ores, characterized by a very simple mineral composition, is pyrite, which is represented by three generations.

Hotite, hydrohotite and hydrohematite, which are hypergene minerals of iron, are observed in the peripheral parts of pyrite grains in the form of rims surrounding them.

Irregularly shaped aggregates of sphalerite, galena and chalcopyrite forming a paragenetic association are often found in the mineralization areas that we conducted our research.

For the first time, we discovered the scale-shaped formation of a special mineral of molybdenum – molybdenite in this zone during the microscopic studies.

Small grains of marcasite, branch- and thorn-like aggregates of pyrolusite, soot-like masses of psilomelane, iron oxides such as magnetite and hematite, minerals of titanium such as rutile and ilmenite, irregularly shaped small grains of iron monosulfide – pyrrhotite are also found in the ores.

CHAPTER IV. MINERALOGICAL CHARACTERISTICS, PETROGEOCHEMICAL PECULIARITIES AND FORMATION CONDITIONS OF TERRIGENOUS-SEDIMENTARY COMPLEXES OF MINERALIZATION AREAS OF THE REGION

4.1. Mineralogical composition of terrigenous-sedimentary complexes

Microscopic examination and analysis of chemical composition of rock samples taken from mineralization areas of the research area show that most of them are represented by sericite-siltstone clay shales, sericite graphitized sandy clay shales, sericite sandstones, aleurolitic sandstones, clayey siliceous siltstone, pyrite sandstone, and other types with mixed mineral composition. Sandstones and clay shales have been altered along faults and areas where flow cleavage has been observed, undergoing intensive graphitization, chloritization, and limonitization. Besides feldspar and quartz grains, relatively coarse mineral crystals of crystalline schists are widespread in

flyschoid sandstones. The main part of the clayey siltstone consists of a siliceous-clay mass in which fine clasts (0.02-0.1mm) of feldspars and relatively rare quartz grains (like quartzite in some areas) are irregularly located.

The siliceous part is represented by cryptocrystalline quartz. Most of the feldspars are pelitized. The main mass of calcareous-clayey siltstones consists of feldspars, quartz, calcite grains and a small amount of calcareous-clayey cement substance. It should be noted that quartz is the most widespread among the non-metallic minerals that accompany ore minerals. The rocks contain a significant amount of clay minerals such as illite, kaolinite, montmorillonite, carbonates represented by calcite, siderite and dolomite, chlorite, hydromica, barite, gypsum, sericite and a number of other non-metallic minerals, as well as monazite, apatite, zircon and some other accessory minerals (Figure 3).

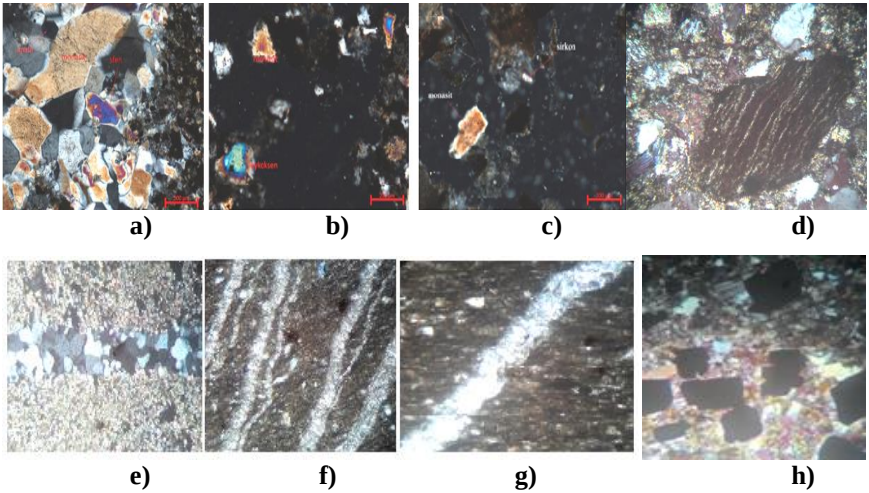

Figure 3. Minerals mentioned in the composition of rocks. In graphitized black shales: a) monazite, leucoxene, apatite and sphene with quartzites; b) leucoxene and monazite; c) zircon and monazite (parallel nicols 10X5); d) coarse mineral crystals of crystalline black shales in the flyschoid formation (parallel nicols 10X5); e) quartz vein cutting dolomite (parallel nicols 10X5); f) and g) epigenetic mineralization in fractures of black shales (parallel nicols 10X5); h) ore sandstone (parallel nicols 10X5).

4.2. Petrogeochemical characteristics of terrigenous-sedimentary complexes

In order to determine the petrochemical peculiarities of the rocks of the aspid and terrigenous-flyschoid formations of the Duruja structural-formation zone and to investigate the origin and sources of the materials brought to the sedimentation basin during the formation process of these sediments, their lithochemical analysis was carried out using the petrochemical modules (hydrolyzate, aluminosiliceous, titanium, femic, sodium-potassium, alkaline, normalized alkalinity, iron) by the method of Y.E.Yudovich and M.P.Ketris and genetic interpretation of the chemical composition of the rocks of the Duruja zone was carried out using Modul, Bakhti, Roser, Korsh, Maynard diagrams[4].

So, according to the petrochemical indicators of sandstones, black shales and siltstones of the Duruja zone and the results obtained from the interpretations made on the models, it was determined that the parent rocks of this region and medium-content subalkaline type volcanogenic-sedimentary materials were transported from the similar sources.

On the other hand, according to the hydrolyzate module, it was determined that most of the rocks we studied belong to clay sediments and their siallite class. High values of aluminosilicate modulus in rocks are due to the presence of hydromics, its low values are due to the presence of pyroclastic feldspars, low alkali modulus, and high iron modulus are associated with the presence of volcanicoclasts, low alkali modulus and high iron modulus are mainly related to the presence of volcaniclasts. Low values of the titanium modulus indicate that the regenerating environment is active during the lithogenesis processes.

4.3. Formation conditions of Middle Jurassic sediments of mineralization areas

In order to study the formation conditions (water salinity, basin depth, climate, etc.) of Middle Jurassic sediments in different areas of the Duruja zone, ratios of some chemical elements (Ti/Mn, Sr/Ba,

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[4] Roser, B.P., Korsch, R.J. Determination of tectonic setting of sandstone-mudstone suites using SiO_2 kontent and K_2O/Na_2O ratio // – Journal of Geology. – 1985. №94. – p. 635-650

Na/K, Na/Ca, Fe/Mn), concentrations of calcium, magnesium and sulfur, as well as aluminosilicate, titanium, sodium, potassium and alkaline modules were used.

Alternation of sandy-siltstone and clayey-shale facies, the results of determining the amounts and ratios of alkaline elements (Na, K, Ca), the investigation of various geochemical modules, sulfur concentration, a regular decrease in the average indicators of Ti/Mn and Fe/Mn ratios give reason to think about the gradual transition of sediment accumulation from coastal and shallow sea condition to relatively deep sea condition in a relatively humid climate. It was determined that the frequent alternation of layers of different thicknesses and lithological composition (sandstone, siltstone, clay shale) in the section of the rocks we studied is related to the change of sediment accumulation conditions as a result of tectonic movements.

CHAPTER V. GEOCHEMICAL CHARACTERISTICS OF ORES AND ROCKS OF DURUJA ZONE

5.1. Mathematical-statistical analyses

5.1.1. Distribution of chemical elements in ores and rocks of model mineralization areas of Duruja zone

Geochemical researches were carried out for clay shales, sandstones and siltstones of the Duruja zone, the analysis results of the samples taken from these rocks and the rock-hosting ores were processed by mathematical-statistical methods (main components, correlation, cluster and factor), and geochemical modeling was carried out based on the obtained data[5]. It was determined by the method of main components that elements such as Cr, Mn, Cu, As, Sb, Cd, Ba, Au, Ag, Ti, Zr, V, Mo, Se, Hf, La, Nd, Lu, Th, U in the black shales, Cr, Ni, Co, Cu, Zn, Pb, Sr, As, Cd, Ba, Au, Zr, La, Sm, Eu, Tb, Th in sandstones, and Cr, Mn, Cu, Pb, As, Sb, Cd, Ag, Ti, Zr, V, Mo, Se, Hf, La, Ce, Nd, U and Cs in siltstones are useful components (major components) of the research area, the total number of components

[5] Поротов, Г.С. Математические методы моделирования в геологии: Учебник / – Санкт-Петербург: Санкт-Петербургский Государственный Горный Институт (Технический Университет). – 2006. – 223 с.

was reduced by excluding less informative components, and further research was conducted on the main components.

In order to check the subordination of the variables – elements to the regularity of normal distribution and to conduct accurately other geological-mathematical-statistical analyses, the statistical parameters (minimum and maximum quantities, numerical mean, median, root mean square deviation, excess, asymmetry, etc.) of their quantities were calculated, and the criterion principles of normal distribution were used to conduct the analyses ($A_s \approx E_s \rightarrow 0$).

A pairwise correlation analysis was performed between the elements selected from the main components and obeying to the normal distribution law.

After determining the relationship in the correlation matrix of these elements, which have a high concentration of Clarke in the rocks of the Duruja zone and are separated as main components, in order to separate the maximally close ones into separate groups due to the similarity of their geological and physico-chemical conditions of formation, groups consisting of elements with high central correlation values were determined using cluster analysis. Black shales are divided into group I (Cu, Mo, As, Ti, V, Cd, Se, Zr, Hf, Nd, U, La, Th) consisting of central Cu-Mo, Ti-V and Cd-Se and group II consisting of Ba, Au, Ag with the help of cluster analysis. 3 groups were determined in sandstones by a similar method: I – Co, Ni, Cu, Zn, Pb, II – Sr, Ba, Au, III – As, Cd. The I group consisting of V, Mo, Cu and the II group represented by Cd, Ti, Se, Nd, and Ce elements were determined in siltstones.

Factor analysis and "Cattel" diagram were used in order to show the factors affecting the accumulation of elements included in the abovementioned groups and to create a description of the distribution forms of similar elements in complex geological objects in the coordinate space. Analyzes were carried out by "STATGRAPH-18" and "STATISTICA-10" software package, factor loadings were determined according to the number of elements.

At the same time, in order to more comprehensively investigate the factors affecting the accumulation of elements, their more contrasting associations were determined by rotating them around the coordinate axis using the Varimax method, the anomalous zones of

elements with high concentration of Clarks and high load in factors I, II, III were identified in the studied samples.

So, high field strength elements of factor I such as Cu, Zn, Pb, Ni, Co, Sr, Au, Ba, Cd, As, factor II such as V, Se, Sb, Mo, Cd, Eu, Tb, Lu, Hf, U and factor III such as La, Eu, Tb, Sm, Cd, Ce, Zr, Th were observed in the rocks of the Duruja zone and the rock-hosting ore minerals by mathematical-statistical methods.

5.2. Mixed elements of ore and non-metallic minerals and their occurrence forms

The distribution of components in ore and non-metallic minerals of the region and their occurrence forms were investigated by different methods (Introduction).

As a result of the conducted research, mixed elements such as V, Cr, Mn, Mo, Sn, Hf, Gd, Se, La, Ce, U, Au, Ag and P were observed in clay minerals. Except for chromium, the abovementioned elements are present as a mechanical mixture. Mixed elements such as Au, Ag and Se were found in globular pyrite aggregates of syngenetic origin, and Au, Cr, Cd, Zn, Ni, Co in epigenetic pyrites[6]. It is assumed that Ni, Co, Se are in isomorphic form in this mineral aggregate (Figure 4).

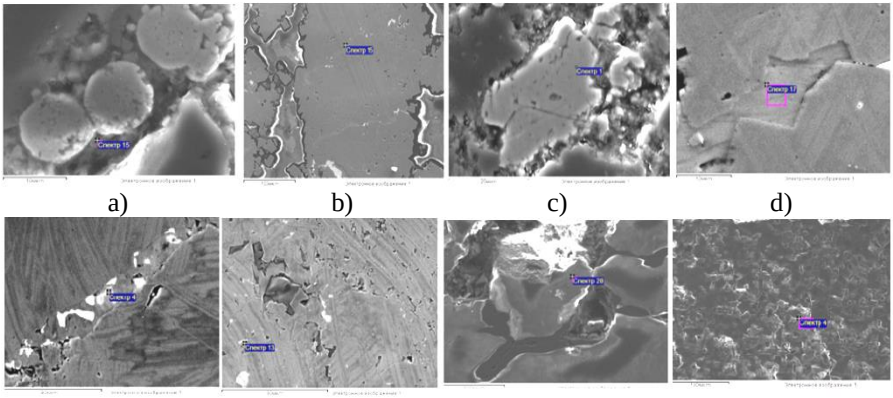


Figure 4. Image of minerals in "SEM" electron microscope. Syngenetic pyrite (a), epigenetic pyrite (b), rutile (c), chalcopyrite (ch), sphalerite (d), galena (e), quartz (a), dolomite (f)

[6] Годовиков, А.А. Минералогия / А.А. Годовиков. – Москва: Недра. –1983. – 647 с.

Mixtures of elements such as V and Sn have been observed in rutile, Cu and Cd in sphalerite and galena, which occurred in the form of paragenetic associations, besides silver with an average amount of 1.01%, Co, Cr and Se in galena, In (1.02%) in sphalerite, and Au, Pb and Cr in chalcopyrite. Some of these elements are observed as isomorphous form (Ag, Se, Cd), while others are observed as mechanical compounds in the abovementioned minerals. Noble (Au, Ag) and nonferrous (Zn, Pb) metals are found in quartz, La, Gd, Sn, Ce, P, Se and other mixed elements are found in carbonates – dolomite and calcite. A much higher amount (1.01%) of one of the rare earth elements, godolinium, was observed in calcite than in dolomite.

The accumulation of rare earth elements and thorium in the rocks of the Duruja zone is related to the minerals such as monazite, apatite, echinite, orthite and zircon observed in them and the weathering products of the rocks where these minerals are located, as well as the sorption properties of clay minerals contained in the black shales. There is no correlation of REE with organic matter in black shales of the region. The absence of lanthanoids in the results of ICP-M analyzes of $C_{org.}$ extracted from black shales suggests that their accumulation is not related to organic matter.

At the same time, as a result of electron-microscopic studies, the participation of a number of radioactive metals, rare and rare earth elements (U, Th, Eu, Hf, Mo, Nb, etc.) in the isomorphous form was determined in apatite, zircon and other mineral aggregates.

CHAPTER VI. FACTORS AFFECTING ORE ACCUMULATION IN THE BLACK SHALES OF THE REGION, GEOCHEMICAL MODEL OF MINERALIZATION AND GEOCHEMICAL ASSESSMENT OF ACCUMULATION POTENTIAL OF THE ELEMENTS OF THE ROCKS

6.1. Factors affecting ore accumulation

Taking into account the possibility of relation of the mineralization of black shales with organic matter, the strong sorption characteristics of clay minerals, and considering that monazite, apatite, zircon and other minerals are carriers of rare earth elements, biogenic and abiogenic sulfur creates an oxidizing-restorative environment, it is of particular importance to investigate the role of organic matter,

sulfur, clay minerals, and accessory minerals in the accumulation and distribution of elements in the black shales of the Duruja zone.

In order to study the effect of $C_{org.}$ on ore accumulation in the black shales of the Duruja zone, tests were taken from these rocks of the model areas, the amount of organic matter in their content was determined, and their dissociation was studied depending on the temperature. As the results of thermographic and pyrolysis analysis, it was determined that the amount of organic matter in these rocks of the mentioned zone varies mainly in the range of 1.35-8.36% (sometimes 9-11%). It is observed that the sediments of the terrigenous flyschoid formation are gradually replaced by the sediments of the black aspid shale formation from N-W to S-E of the research area, and the amount of organic matter in the rocks increases in this direction.

In order to determine the type of organic matter in the rocks, the "Fourier" IQ spectrogram of the organic part that was separated by extraction was created, and according to the results of the analysis, it was found that it consists of various organic associations – bitumoid (Ẋ=2,3%), graphite (Ẋ=3,6%), fulvic acid (Ẋ=2,1%) and humic acid (Ẋ=3,8%). A positive correlation was observed between the organic matter and the amounts of V, Mn, Ni, Se, Mo, Cu, Cd, Ag, Ti, Nd, Hf, Th, U and sulfur in the black shales of the Duruja zone. In order to determine which of the abovementioned elements are accumulated in the organic matter, the extracted organic matter was studied in an ICP-MS (NexION 300D) inductively coupled mass spectrometry with argon plasma, and besides the predominant Se, V, Mo, P, S, U, Au and Zn, small amounts of elements such as Sr, Ba, Cd, Ti and Ag were also found in its composition.

The accumulation of rare earth elements, which are sorption products in the clay minerals (mainly in montmorillonite) of the zone where we conducted the study, in high concentrations shows that the process of sedimentation took place at a low speed for a long time.

Besides the sorption in the rocks, the desorption process also took place in different environments (sour, alkaline, etc.).

As a result of our long-term experiments on the samples taken from the model mineralization areas of the Duruja zone, it was determined that Cu, Zn, Co, Ni and Ag ions are almost not desorbed from the

studied rocks in alkaline and neutral environment[7]. This process mainly occurs in an acidic (pH=3) environment, especially due to the sulfuric acid formed as a result of the erosion of pyrite. So, solutions moving as a result of desorption are enriched with many components and vice versa – here the concentration of these components decreases, causing negative anomalies. As a result of subsequent migration of enriched solutions, the concentration of elements in rocks increases due to sorption in other zones, and as a result, positive anomalies are formed.

Besides sorption and desorption in the studied clay shales, processes such as geosorption, adsorption, and hemosorption also play an important role in the formation of mineralization zones. In connection with the formation of an oxidizing-restorative environment in clay shales, which host biogenic sulfur and sulfurous compounds from hydrothermal vents transported by deep faults and other minor faults in rocks subjected to tectonic processes, the sedimentation of a number of elements and the process of endogenous mineralization occur due to H_2S. A positive correlation between the amount of sulfur and the concentrations of some elements – Pb, Zn, Cu, Mn, Ni, Co, As was observed in the black shales of the Duruja zone.

So, it was determined that 3 factors play an important role in the accumulation of the abovementioned elements in the black shales of the Duruja zone – the amount of organic matter, clay minerals in the rocks, and the high oxidizing-restorative potential of the mineralization environment, which is favorable for the formation of endogenous ores related to hydrothermal processes.

At the same time, it was found that the irregular accumulation of the abovementioned elements in the mentioned rocks depends on hydrochemical processes and the degree of sorption of ore-hosting rocks.

6.2. Isotopic composition of sulfur in sulfides of the Duruja structural-formation zone

Investigating the source of ore matter is one of the important theoretical and practical issues of mineralization. It is known that ac-

[7] Кашкай Ч.М, Зейналова С.А., Керимов Р.В., [и др.]. Экспериментальное исследование процессов концентрирование меди, цинка, кобальта, никеля и серебра в черных сланцах Дуруджинской зоны южного склона Большого Кавказа (Азербайджан) // Воронеж: Вестник Воронежского Государственного Университета. Серия: Геология. – 2017. – № 2. – с. 91-96

cording to the results of the analysis of the isotope composition of sulfur in the sulfides, it is of particular importance to correctly direct the exploration work in determining the source of the ore matters.

In order to investigate the ore genesis of the Duruja zone, the isotope composition of sulfur in pyrites of different morphological characteristics, which was taken from the ores and ore-hosting rocks of mineralization areas, was analyzed (Figure 5).

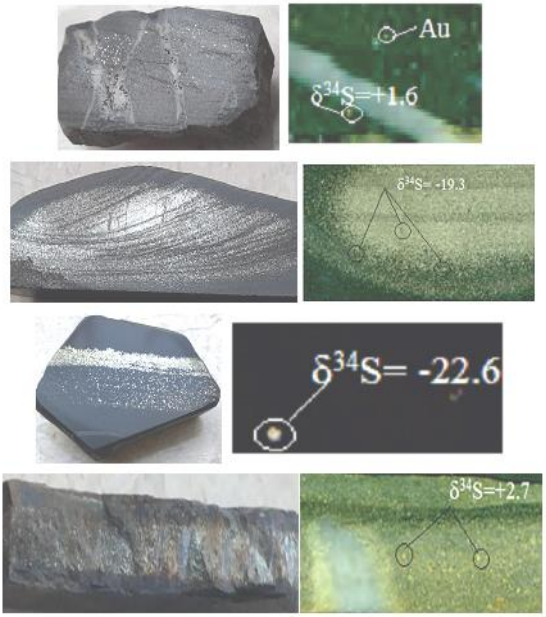


Figure 5. Isotopic composition of sulfur in pyrites of different morphologies in ores and ore-hosting rocks of the Duruja zone

The variation range of $\delta^{34}S$ in pyrites extracted from the samples taken from rocks and ores located between separate branches of transverse faults of different sizes, which complicate the geological structure of the Duruja zone besides the Ganar and Zangi deep faults, varies between +3.2 and +6.7 ‰, but in pyrites extracted from the samples taken from black shales varies between -18 and -22.6 ‰[8].

[8] Виноградов, В.И. Роль осадочного цикла в геохимии изотопов серы / – Москва: Наука. –1980. – 192 с.

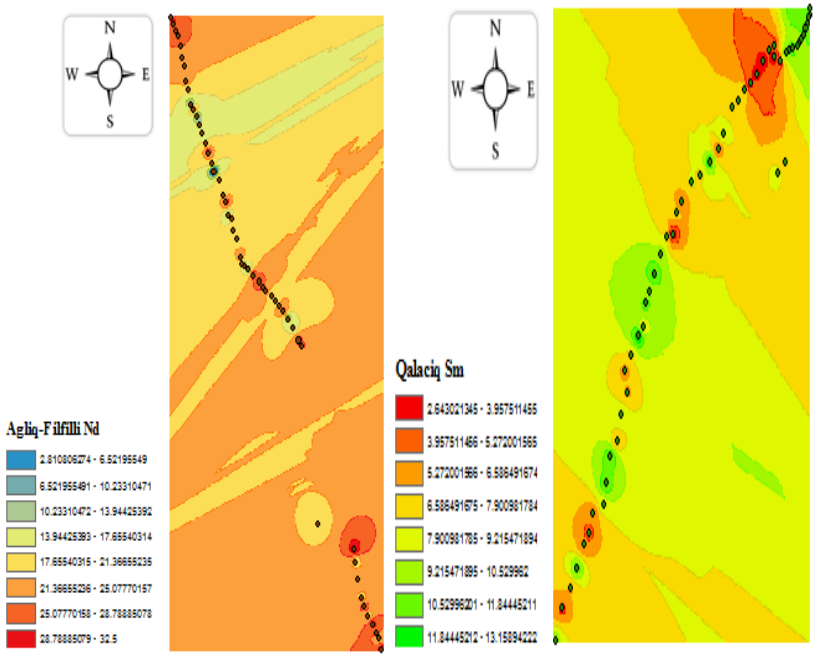
The results of the isotope analysis show that the sulphides of the mineralization areas of the Duruja structure-formation zone are related to two sources: a) biogenic ores, mainly formed with the participation of bacterial activity in early diagenesis; b) juvenile sulfides, formed in connection with depth faults. As can be seen in Figure 5, small grains of gold are found near endogenous sulphides in such zones.

It should be noted that the rocks of geochemical anomalous zones of different origins of the mentioned zone differ from each other according to their element composition.

6.3. A geochemical model of mineralization

The data (collection of chemical elements depending on physico-chemical and geological conditions in samples taken by recording GPS coordinates) we obtained as a result of our geochemical research were analyzed and modeled by the "ArcGIS" computer program, and models reflecting the distribution of each of the studied chemical elements in mineralization areas were built .

Some of these models are showh in picture 6.



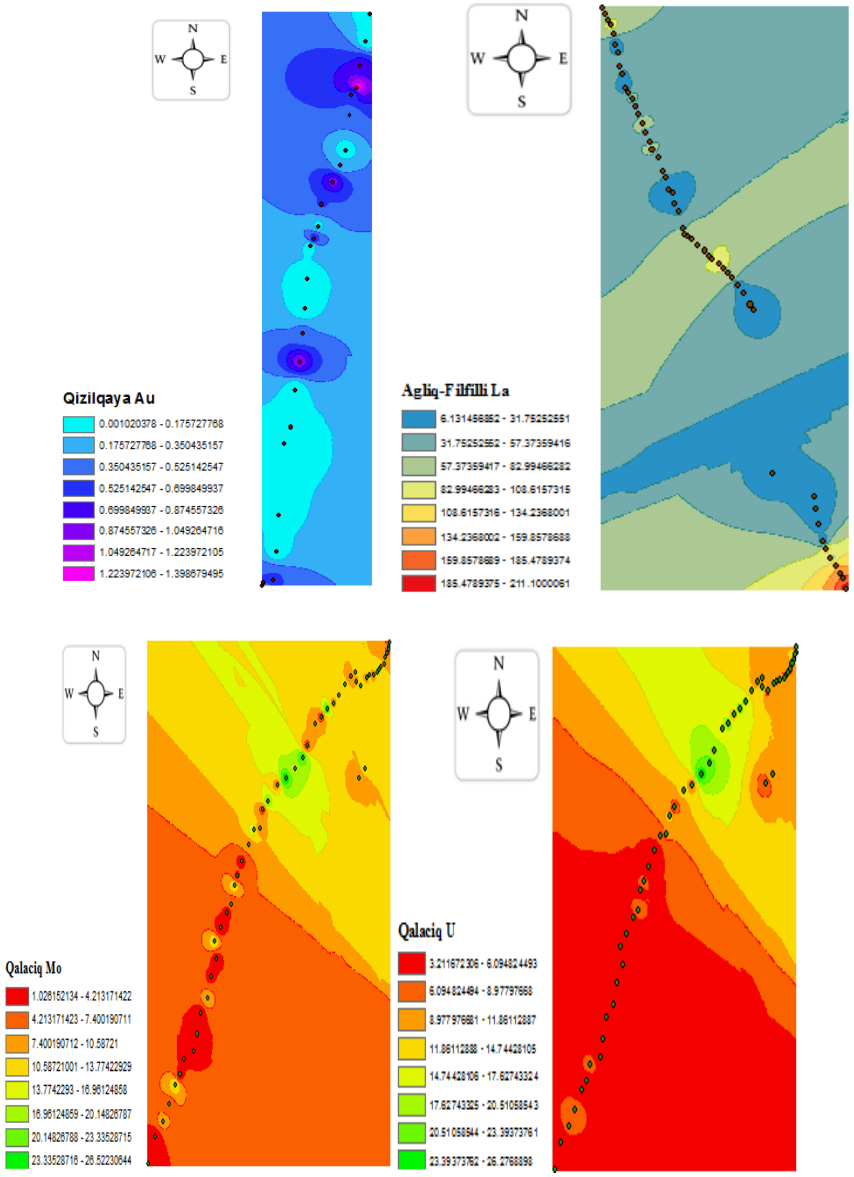


Figure 6. Distribution model of chemical elements characterised by high concentration of ore mineralisation ares

Using the mentioned models, anomalous zones where elements characterized by high concentration values observed in mineralization areas were determined.

6.4. Geochemical assessment of the potential of the rocks of the model mineralization areas to accumulate noble, non-ferrous, radioactive metals, rare and rare earth elements

Prospective anomalous areas for elements such as Pb, Cu, Zn, Ni, Co, Cd, V, Zr, La, Ce have been determined in the neighborfault areas of the Gaynar fault in the north and Zangi faults in the south in **the Gum-Lekit mineralization area** (Figure 7).

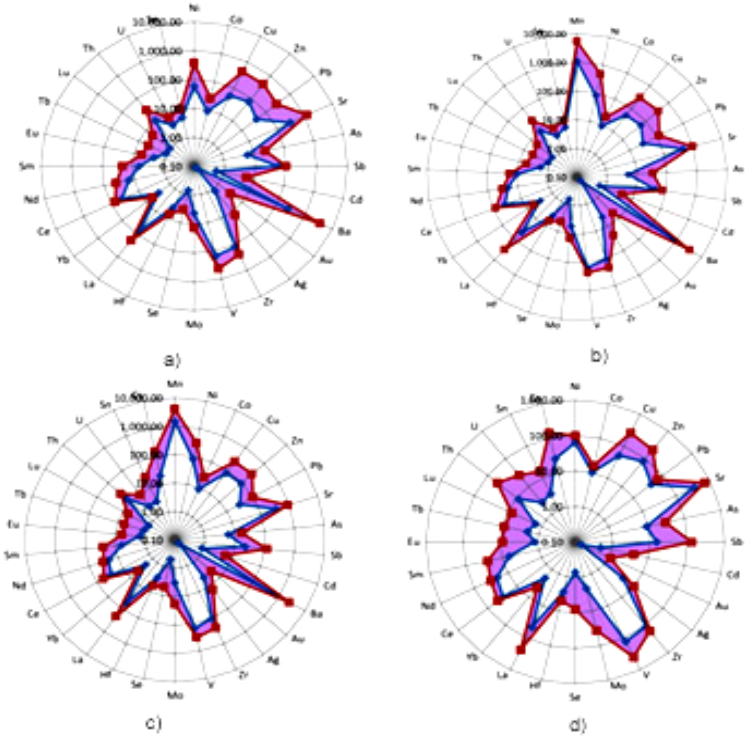


Figure 7. Statistical distribution diagram of mixed elements in the rocks of Gum-Lekit (a), Gizilgaya (b), Aglig-Filfilli (c) and Galajik (d) mineralization areas

Average amount
numerical averages of very high local values
areas with local high values

The Gizilgaya mineralization area is promising for Au, Cu, As, Zn, relatively little La, Yb, Ni and Co, and anomalous zones of these elements are observed in the north – in the neighborfault areas of the Gaynar fault.

The Aglig-Filfilli mineralization area differs from other model areas by the diversity of the spectrum of chemical elements and their high concentrations in ore and rocks. While studying the formation conditions of the rocks, it was found that this area was exposed to diversity due to its location between the coastal and deep sea conditions and the repetition of oscillating movements. Anomalous zones, which are considered promising for the search for elements such as Au, Ag, Cu, As, Se, Mo, V, Sb, La, Se and Nd, have been distinguished in Gaynar fault in the north, Zangi fault in the south and in the center of this area, where there are numerous transverse and longitudinal faults in the research area.

The rocks of **the Galijik mineralization area** are distinguished from the sediment of other model areas by the fact that they consist of monotonous clay shales containing a higher amount of organic matter. Although some elements (Au, Mo, U, Se) are identified as forming anomalous zones throughout the area in the models, anomalous zones promising rare earth elements are more evident in the neighborfault area of the Zangi fault located in the south.

Statistical models were created in order to assess the accumulation potential of the abovementioned elements of the rocks in the Gum-Lekit, Gizilgaya, Aglig-Filfilli and Galajik mineralization areas, which are located sequentially from the northwest to the southeast of the Duruja zone and taken as a model.

The models were created according to the difference between the average values of the maximum standard declination of the elements observed in the rocks at the site and the average values of the elements at the site: the high difference indicates that they have local anomalous values.

So, according to the data obtained from the models we compiled based on the results of actual materials, the rocks of the Duruja structural-formation zone are characterized by high potential in terms of accumulation of noble, non-ferrous, radioactive metals, rare and

rare earth elements, and the mentioned zone is considered as a sufficiently promising region for searching for these elements.

CONCLUSION AND SUGGESTIONS

1. The process of ore formation in the Duruja structure-formation zone is represented by two stages of mineralization. The first stage is characterized by the ore formation consisting mainly of early syngenetic pyrite, and the second stage is characterized by the formation of epigenetic sulfides related to the activity of hydrothermal solutions.
2. According to the petrochemical indicators, it was determined that the materials brought to the sedimentation basin are genetically related to the basic and medium subalkaline content of volcanogenic materials, most of the rocks of the Duruja zone are represented by clayey sediments that belong to the sialite class, and the activity of the regenerative environment plays an important role during the lithogenesis processes.
3. The distribution and accumulation regularities of chemical elements characterized by high concentration in the Duruja zone have been determined, and it was found that the mixed elements such as Cd, Au, Co, Ni, In, Ag are accumulated in ores, V, Cr, Sn, Mo, La, Hf, Ce, Au, P in clay minerals, La, Gd, Sn, Ce, P, Cr, V in carbonates, Mo, V, Se, S, P, Au in $C_{org.}$ extracted from black shales and their occurrence forms were investigated.
4. The dependence of different aspects, which were found in the amounts and spectra of the studied elements in separate zones of different mineralization fields, on the lithological composition of the rocks, their degree of sorption, hydrothermal alteration occurring in small fault zones, and the intensity of syngenetic and epigenetic mineralization processes was determined. A direct dependence of the metal composition of the rocks of the black shale formation on the intensity of occurrence of sulphide mineralization associating them was revealed.
5. Anomalous zones are separated, where high concentrations of Cu, Zn, Pb, Ni, Co, As, Au, Ag, Ba, Sr, La, Ce, Eu, Tb, Zr, Th and

high concentration of Cu, Mo, V, Se, S, P, Sb, Cd, Eu, Tb, Lu, U in black shales rich in organic matter are observed in the neighborfault zones of the Gaynar depth fault in the north of Gum-Lekit, Gizilgaya, Aglig-Filfilli mineralization areas and Zangi depth faults in the south in the Galajik mineralization areas and in their intersection areas with transverse faults, their geochemical, mathematical-statistical models were compiled, the criteria for the prediction and investigation of blind ore body were developed.

6. According to the results of the conducted research, it is suggested to carry out exploration works in the zones accompanied by anomalous values of Cu, Zn, Pb, Ni, Co, As, Au, Ag, Ba, La, Ce, Eu, Nd and Tb in the intersection areas of the Gaynar and Zangi faults with transverse faults, by anomalous values of Cu, Mo, V, Se, Sb, Cd, Eu, Tb, U in black shales rich in organic matter.

The main provisions of the dissertation are reflected in the following scientific works:

1. Gadirova, T.S. Mathematical modeling of the geochemical characteristics of the Gizilgaya ore field (Duruja seaming zone) // - Baku: Gənc Tədqiqatçı, - 2020. Volume VI, No. 1, - p. 63-72 (in Azerbaijan)
2. Gadirova, T.S. The role of $C_{org.}$ in the accumulation of some chemical elements in the black shales of the Duruja structure-formation zone // - Baku: Baku State University News; Natural Science Series; - 2022. No. 4, - p. 81-91. (in Azerbaijani)
3. Gadirova, T.S. Mineral composition of ores and rocks of the Duruja structure-formation zone // - Baku: News of Azerbaijan Higher Technical Schools, - 2022. file 23, - p. 137-145. E-ISSN: 2674-5224, DOI: 10.36962/PAHTEI, 12 (in Azerbaijan)
4. Gadirova, T.S. Mineralogical and geochemical characteristics of black shales of Duruja structure-formation zone. Materials of the Republican Conference "Geology: problems, prospects". - Baku, May 05-06, 2022. pp. 123-125 (in Azerbaijan)
5. Gadirova, T.S., Kerimov, R.B. Mineralogical and geochemical features and ore-bearing prospects of black shale formations of the Duruja structure-formation zone of the eastern segment of the Greater Caucasus (Azerbaijan) // Ekaterinburg: International Sci-

entific Research Journal, 2023. No. 4 (130). pp. 1-11. // DOI: https://doi.org/10.23670/IRJ.2023.130. p. 96 (in Russian)
6. Kerimov, R.B., Gadirova, T.S., Shikhova, L.F. “Mineralogical and petrographic features of gold ore occurrences of the Duruja anticline on the southern slope of the Greater Caucasus // Collection of reports - IX International Scientific and Practical Conference “Integration Processes of World Science in the 21st Century” Russia: - Kazan. - 2014 - pp.100-104 (in Russian)
7. Kerimov, R.B., Samedova, R.A., Gadirova, T.S. Petro-geochemical features and ore-bearing prospects of the Cretaceous volcanogenic complexes of the Vandam zone of the southern slope of the Greater Caucasus // - Riga: Monthly international scientific journal “SCITECHNOLOGY”, - 2018, No. 10, - pp. 7-10 (in Russian)
8. Kerimov, R.B. Mineral composition and geochemical features of the ores of the Filfilli gold ore occurrence of the Druja seaming zone (Azerbaijan) / R.B. Kerimov, R.A. Samedova, R.S. Jafarova [etc.] // Periodical collection of scientific works, Third All-Russian Scientific Conference September 15-17, 2014, (Issues of geology and integrated development of natural resources of East Asia) volume 1, Blagoveshchensk - 2014 - p.105-106 (in Russia)
9. Samedova R.A., Jafarova R.S., Gadirova T.S. Volcanism and metallogeny of the Vandam structure-formation zone of the Southern slope of the Greater Caucasus. VIII International Conference “Biosphere Volcanism and Environmental Problems. G. Maykop, Adigey State University. 2016 pp. 156-157 (in Russia)
10. Gadirova, T.S. Textural-structural characteristics and mineral types of ores of the Aghlig-Filfilli mineralization area of the Duruja zone // Journal of Geology, Geography and Geoecology 32 (1), 017-025. doi:10.15421/112302-2023. - p. 17-25 (in English)
11. Gadirova, T. S. The geochemical features of the black shales of Duruja zone of the Greater Caucasus and their prospects of the ore mineralization // VII international conference of young scientists & students. Information technologies in solving modern problems of geology and geophysics. - Baku. - 2018. - p.117-118 (in English)

12. Kerimov, R.B., Gadirova, T.S. The investigation of the possibility of leaching noble metals from black shale complexes that contain gold of Duruja zone (Azerbaijan) // Monthly international scientific journal "LINGVO-SCIENCE" Bulgaria, - Varna, No. 11, - 2018. - pp. 3-7 (in English)

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