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# MINERALOGY AND FORMATION CONDITIONS OF BARITE-POLYMETALLIC MINERALIZATION BASIN WADI AL-MASILA (REPUBLIC OF YEMEN)

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**ABSTRACT OF
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PhD. OF GEOLOGICAL-MINERALOGICAL SCIENCES**

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## GENERAL DESCRIPTION OF WORK

**Actuality of work.** The thesis is devoted to the reproduction of the mineral resources basin of Yemen, in particular, metallic and non-metallic minerals. Yemen occupies the southern part of the Arabian Peninsula, and geologically includes of the Nubian-Arab platform, and consist of various kinds of complex rocks, such as, metamorphic, igneous and sedimentary rocks, distributed in different age groups from the Precambrian to the Cenozoic. The territory of the Republic of Yemen is perspective in many kinds of resources, which have economic importances, because these objects are involved in the provision of financial revenue to the State Treasury of the Republic of Yemen. The object of Wadi Al-Masila which mentioned in the present work is located in the east of the Republic of Yemen. This is important, because it contains a wide range of metallic minerals such as lead, zinc, manganese and others, beside a whole range of non-metallic minerals, particularly barite. Barite is listed as highly deficit minerals, and is used in many industries in particular when drilling operations of oil companies.

**Degree of the problem elaboration**. Barite deposit in the basin of Wadi Al-Masila discovered relatively recent and many of the issues of its geological structure and origin is not fully resolved. The object of development is only barite. Although high concentrations of ore elements, industrial value polymetallic not clear yet and requires a detailed mineralogical and geochemical studies. In 2003 - 2004 were conducted geological, mineralogical and geochemical studies in the area of mineralization and hydrothermally altered rock, led by Professor MA Mattasha and geologist AA Al-Ameri using geological, geochemical, geophysical and drilling operations. The most intensive exploration work on a deposit were carried out from 2005 to 2010. Since 2011 mineralogical and geochemical studies were continued by geologist M.A Al-Hajj in the period of study postgraduate at Kazan Federal University and formed the basis of this thesis.

**Object of researches**. The main object of the study is the minerals of hydrothermal-sedimentary barite-polymetallic mineralization basin of Wadi Al-Masila, localized in the Mesozoic rocks.

**Goal and research problems**. The goal of the work is to study the material composition (mineral and chemical) and formation conditions of barite-polymetallic mineralization basin of Wadi Al-Masila.

To achieve this goal, the following problems were solved:

1. The study of the mineral and chemical composition of the ore;
2. Study of the nature of changes in the near-ore rocks;
3. Study the crystal chemical peculiarities minerals, ores;
4. The study of the morphology of minerals and parageneses;
5. Establishing stages of mineralization;
6. Figuring out conditions for the formation of ore bodies;

**The scientific novelty of the work is as follows**:

1. For the first time, ore minerals deposits studied with complex methods , allowed to reveal their structural, morphological and physico-chemical features of the formation;

2. For the first time, investigated the mineralogy of near ore metasomatic rocks and the regularities of spatial distribution of near vein changes;

3. Established forms of trace elements occurrence in ores. For the first time by electron microscopy revealed the presence of chloride in the ores of lead deposits - mineral kotunita PbCl2;

4. Established typomorphic signs major ore minerals and assessed their genetic information content;

5. For the first time, performed radiation estimation of ore samples and found the presence of radium isotopes 226 and thorium-232, which are products of uranium decay;

6. For the first time, using the method studied termobarogeochemical gas-liquid inclusions in the main vein of minerals and evaluated their formation temperature;

7. Identified the main parageneses of ore-forming minerals that are typical for different time intervals forming mineralization, and established the sequence of their release;

**Theoretical and practical significance of the work**. As a result of this work revealed basic regularities of formation of hydrothermal-sedimentary complex barite-polymetallic ores. Established paragenetic relationships minerals in mineralization and the main association of ore minerals. Developed for staging formation barite-polymetallic mineralization basin of Wadi Al-Masila with definite temperature range of manifestation of hydrothermal processes and ore deposition. The results can be used for prediction and the search deposits of a similar type on adjacent areas.

**Methods of study**:In the process, to achieve the goal of the thesis we used a number of modern physical and chemical methods of investigation of the mineral composition. The studies were conducted in two phases. In the first phase the study of minerals and parageneses carried out in laboratories in Yemen and Europe (Hannover, Germany), also ALS Chemex Laboratory in Vancouver, Canada. The second phase was experimental research in Kazan Scientific Center (KFU, ЦНИИгеолнеруд) and National University of Tadjikistan, Dushambe, including sampling studies using physical and chemical methods.

**The main defense points/**

1. The mineral composition of barite-polymetallic mineralization basin of Wadi Al-Masila (Republic of Yemen) has a complex structure and is represented by sulphate, carbonate, sulfide, oxide and silicate mineral compounds, the formation of which is associated with the crystallization of solutions and metasomatic transformations of the surrounding sedimentary rocks as a result of hydrothermal activity and supergene processes. Total on a deposit found and studied for more than 25 mineral types.

2. Typomorphism barite due to the presence of the mineral structure of the paramagnetic defect centers (SO43-, SO3-, O-, SO4-, SO2-, etc.), Arising from the isomorphic replacements and artificial and natural radiation exposure, the latter of which has a profound nature and due to the presence of hydrothermal solutions hypogenic

components containing radioactive decay products of uranium. barite Typomorphism allows to identify its genesis and history of radiation.

3. Formation of the main mineral assemblages reflects the pulsating nature of the mineralization of hydrothermal activity during the formation of Red Sea rift. The temperature range of formation of hydrothermal mineralization according to thermometry study, was 312 - 174 ° C.

**The degree of reliability and approbation of work**. High degree of reliability due to the direct participation of the research of the author in the work on the study of the geological structure of the territory, since the field phase. According to the results field studies was composed of geological map of the area of mineralization and the geological section of the deposit, using the group Robertson map as a basis . The geological structure of the deposit, mineralogical, geochemical, petrographic study of samples of ores and rocks near-ore, also typomorphic and morphological characteristics of ores are studied by the author.

***Approbation of work***. The main positions of the dissertation were presented at the final conference of KFU, as well as international, national and regional meetings and conferences.

***Publications***. On the topic of dissertation published 10 publications, including 2 articles in journals from the list of HAC.

***The structure and scope of work***. The dissertation consists of an introduction, six chapters and a conclusion. The total amount of work is 132 pages, including 58 figures, 9 tables and a bibliography of 110 titles.

**Acknowledgement**

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## MAIN CONTENT OF WORK

### Introduction

Described Actuality of work, the degree of elaboration of the problem, the object of study, designated purpose and objectives of the study, the method and technique of research, formulated scientific novelty, theoretical and practical significance of the work protected by the provisions. It is shown that the degree of reliability and testing operation, noted the personal contribution of the author, given thanks.

**Characteristic of Wadi Al-Masila** (Fig.1). The territory of Yemen is located in the southeast of the Arabian-Nubian Shield, formed in Precambrian times. Metamorphic and igneous rocks of Archean-Proterozoic basement are structural fragment Precambrian mobile belt. They are overlied by sedimentary cover, folded clastic and clastic-carbonate rocks of the Phanerozoic. The sedimentary cover consists of Paleozoic, Mesozoic and Cenozoic formation of (Table 1). Paleozoic appeared only in the north-western part of Yemen. Mesozoic formations are represented by Jurassic and Cretaceous systems, folded marine clastic and calcareous clastic sediments unconformably overlie the Paleozoic sediments. The Cenozoic formations including Paleogene, Neogene and Quaternary sediments.

Tectonic structure of the Republic of Yemen is characterized by large blocks of Archean-Proterozoic basement, cutting by NW-SE direction rift grabens system Marib-Shabwa, which borders the south and west of the rift system of the Gulf of Aden and the Red Sea.

Yemen is characterized by a significant number of metal and non-metallic deposits. From the non-metallic minerals in the sediments of Mesozoic carbonate rocks encountered (limestone, dolomite, chalk), gypsum rocks, marbles, bituminous shale, mineral salts. From the metallic minerals, the most important is lead-zinc mineralization. The largest ore occurrences are complex lead-zinc-silver (Pb-Zn-Ag) mineralization Jabali District. Tobak is located approximately 360 km east-northeast of Aden and the basin Wadi Al-Masila located in Al-Mahra province. Barite-polymetallic mineralization in the basin of Wadi Al-Masila is the main object of the study in this thesis.

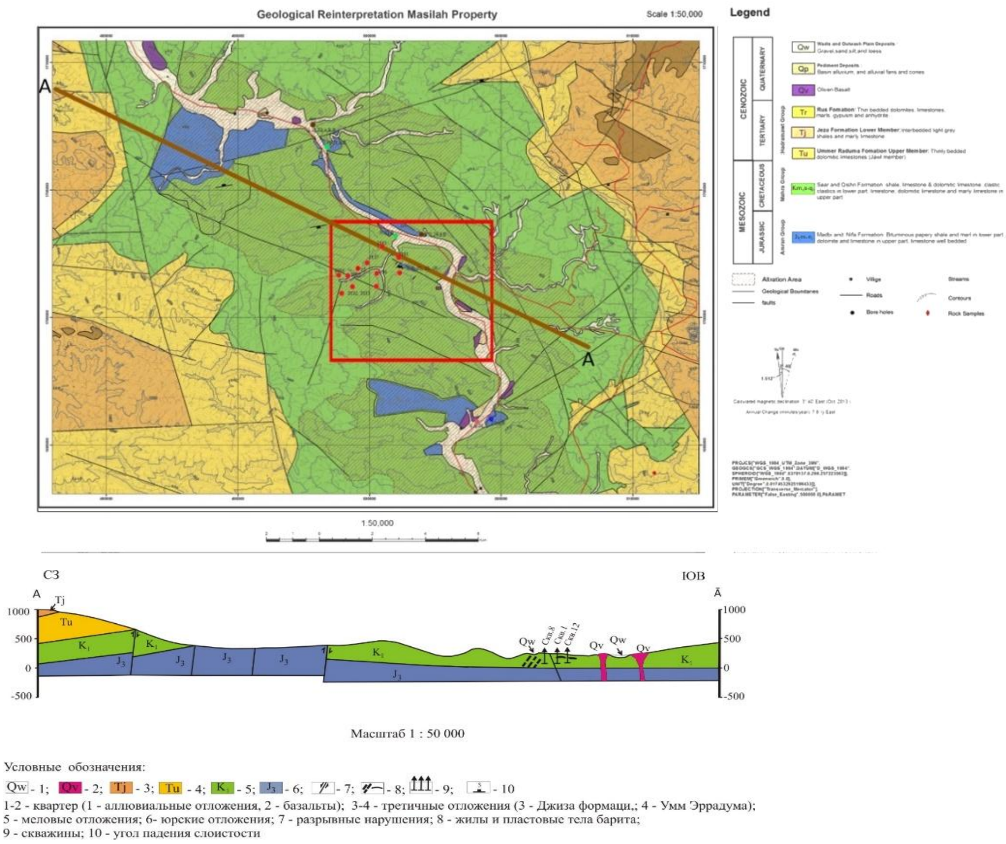


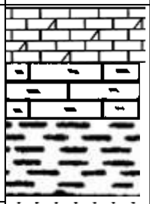
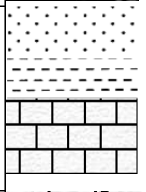
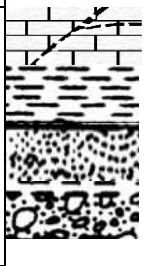
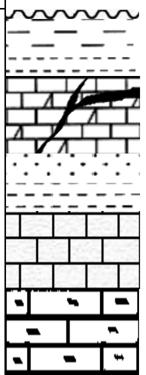
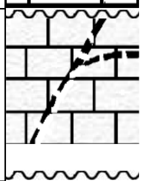
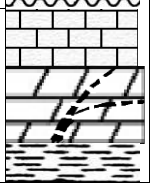

Fig. 1. Geological map and scheme sampling manifestations barite-polymetallic mineralization in the basin of Wadi Al-Masila

## 2. The methodologies of experimental research

In the process, to achieve the goal of the thesis we used a number of modern physical and chemical methods of research of mineral matter. Studies were carried out in two stages. In the first stage, the study of minerals and parageneses carried out in Yemen and European laboratories ALS Chemex Laboratory (Vancouver, Canada) and geochemical laboratory (Hannover, Germany). The second stage of the experimental work was performed in the laboratory of the Kazan Federal University and included the study of physical and chemical methods of ore samples. As a result of petrographic and **mineralographic** studies, we identified the mineral composition of selected samples, as well as the form and the relationship between the crystals, also to clarify the generations and stages of formation of the deposit.

Table. 1

Lithology-stratigraphic scheme of the sedimentary Basin of Wadi Al-Masila

| System | Series | Stage | formation | lithological column | Thickness м | indexes | Lithological description |
|---|---|---|---|---|---|---|---|
| **Paleogene** | Upper Paleocene - Lower Eocene | | Umm Er-Raduma formation |  | 215 | *Pg* | Dolomitic limestone, marl limestones, argillaceous shales foliated |
| **Cretaceous** | Upper | Upper Cenomanian - Turonian campaign | Mukalla formation |  | 165 | $K_2$ **(***s+t***)***-km* | sandstones and siltstones with interbedded limestones |
| | Lower | Hauterivian - Upper Barremian | Qishn formation |  | >100 | $K_1$*br-g* | Complex of of carbonate rocks consisting of limestone interbedded with shales and sandstones;<br>Complex of clastic rocks consisting of sandstone, shale conglomerate |
| | | Berriasian-valanginion | Saar formation |  | >198 | $K_1$*v-b* | ***Gail:*** reddish calcareous argillite, siltstone, sandstone, slate gray with fossils and interbedded dolomite limestone;<br>***Kalana:***<br>limestones.<br><br>***Samarmar:*** marly limestone and marl |
| **Jurassic** | Upper | Upper titon-lower Berriasian | Naifa formation |  | 149 | $J_3$*b-tt* | Limestone, light gray, layered |
| | | Kimmeridgian - Lower Tithonian | Madbi formation |  | 240 | $J_3$*tt-km* | Bitumen, foliated clay shales, marl, dolomite and limestone |

**Legend**

- limestone, marly limestone;
- dolomitic limestone;
- sandstones and siltstones;
- conglomerate;
- supposed barite veins;
- shales;
- dolomite;
- mudstone and siltstone;
- barite veins;

## 3. Mineralogical and geochemical characteristics of the barite-polymetallic mineralization basin of Wadi Al-Masila

Deposit Wadi Al-Masila in composition ores can be attributed to a complex barite-polymetallic type. Currently, it is being developed exclusively for the production of raw material barite. The industrial value of polymetallic in it has not been used yet.

***Forms of manifestation barite-polymetallic mineralization***. Barite-polymetallic mineralization is concentrated in the area of alteration approximately 300 $km^2$. Mineralization covers the whole sedimentary sequence, forming a maximum concentration in carbonate rocks of Cretaceous period especially in the Saar formations. In all deposits within the Wadi Al-Masila there are 3 varieties ore bodies: 1) bedded (stratiform) body, 2) associated with these stratified-lenticular ore bodies and 3) crosscutting veins. The most perspective areas for the development of barite mineralization is concentrated in tabular (stratiform) deposits. The character of occurrence of ore bodies shows that their formation took place in stages, during the period from the Middle Jurassic to the Paleogene.

***Structure and mineralogical zoning of ore bodies***. All barite-polymetallic body basin Wadi Al-Masila characterized by a zonal structure, due to the peculiarities of the distribution of mineralization therein.

*Bedded (stratiform)* of the body (4.0-6.0 m) usually virtually monomineral. The main components of the mineral phase is barite. According to the study of chemical samples in their content of BaO is up to 67, 00%, SO3 - up to 30, 2%, SiO2 - up to 1,89%, Fe2O3 - to 9.39%. All other elements are present in amounts less than 1.0%. The veins are dominated by aggregates, composed by large, white barite crystals.

*Stratiform -lenticular ore bodies,* as well as stratiform, characterized by complicated structure. They are composed of different size and ellipsoidal flattened lenticular barite units located in carbonate rocks. The thickness of stratified lenticular ore bodies are small up to 1.0 m.

*Crosscutting barite-polymetallic ore bodies* are represented by two main forms of manifestation: veins and stockworks. The veins are usually characterized by subvertical and steeply inclined bedding. Subvertical vein ore bodies are rich in metals. Thus, when the content of BaO to 64,43%, PbO is 11.10%, and ZnO - 0,87%. Barite veins are rich in ore minerals, the most developed galena and sphalerite.

Vertical barite-polymetallic veins, crosscutting bedded stratiform barite body areas are outlined by brecciated host rocks with thickness up to 1.5 m. Stockwork type mineralization is specific to the areas of carbonate rocks, where a dense network of fissures with small-amplitude displacement or no displacement was previously formed. According to chemical studies in samples, $SiO_2$ content reaches 25,5%, Fe2O3 - to 30.27%.

***Mineralogy and geochemistry of barite-polymetallic ores in Wadi Al-Masila.*** Barite-polymetallic mineralization is characterized by a wide variety of mineral composition and represented by carbonate, sulfate, sulfide, silicate and oxide compounds. (By the time of formation, minerals can be divided into synagenetic and epigenetic). The general scheme of mineralization mineralogy is presented in Table 2.

Table 2.

The general scheme of the mineral composition of barite-polymetallic mineralization Wadi Al-Masila

| rouping mineral composition (right) and the degree of quantification (bottom) | Minerals | |
|---|---|---|
| | Non-metallic | Metallic |
| Major hydrothermal<br>(Syngenetic) | Barite<br>Calcite<br>Quartz | Galena<br>blende<br>Pyrite<br>Chalcopyrite |
| Secondary and rare<br>(Epigenetic) | Celestine<br>Gypsum<br>Anhydrite<br>Dolomite | cerussite<br>Anglesite<br>wulfenite<br>Gidrotserussit<br>Smithson<br>Willem<br>hemimorphite<br>Dekluazit<br>vanadinite<br>Cotugno |

**The main non-metallic minerals** of mineralization are barite, calcite and quartz.

**Barite $BaSO_4$** is the main and most common mineral veins. It forms large veins and small veins. In microscopic studies of barites, two generations: 1) in the form of an elongated tabular form of independent precipitates; and 2) in the form of fine aggregates, filling veins and alternating with other minerals. Barite of the second generation is usually associated with quartz and dolomite.

**Calcite $CaCO_3$** is also one of the most important vein minerals in the field. Calcite is formed at various stages and occurs mainly as a vein mineral and as a product of recrystallization of the original mineral substance.

**Quartz $SiO_2$** in the deposit fills cavities and voids in rocks, where it is present in the form of drusoid aggregates composed of smaller euhedral crystals.

**The main ore minerals.** Ore minerals can be divided into hypogenous and hypergenic under the conditions of formation. Hypogenous ores are represented by sulfides - galena, sphalerite and pyrite. Hypergenic minerals are mainly products of the transformation of vein minerals and minerals of host rocks. The composition of ore minerals is very complex and represented by carbonates, sulphides, oxides and sulfates.

**Galena PbS** is found in paragenetic association with barite and forms large crystals and crystal nests in barite veins, which are unevenly distributed in the barite aggregate. Cerussite, anglesite and other sulfates and oxides were formed as a result of oxidation.

**Sphalerite ZnS** forms small and large crystals. For the most part, they are oxidized, which is clearly distinctly apparent in color changes - from yellowish and reddish to black. A variety of color shades of sphalerite crystals refers to the isomorphous replacement of zinc by Mn, Fe, and Cd. The size of sphalerite crystals varies in a wide range - from microscopic to 3 cm.

**Pyrite $FeS_2$** occurs much less often, as a rule, in the form of single crystals or fine-grained precipitates in dolomites or barite aggregates composing veins.

**Chalcopyrite $CuFeS_2$** occurs in the form of phenocrysts in sphalerite crystals and grains of smaller spherical shape closer to the sphalerite boundaries. Emulsions of chalcopyrite in sphalerite indicate relatively high crystallization temperatures. In addition, chalcopyrite is found as a thin dissemination in host dolomites.

**Secondary and rare minerals.** Besides the main minerals in the composition of the ore bodies meet secondary and rare minerals representing sulfide, oxide, sulphate and chloride compounds of lead, zinc, and iron, manganese and other metals. Below is a brief description of them.

1). Ore minerals:

a) **zinc minerals** constitute a large group. Their formation is usually associated with the oxidation of sphalerite.

**Hemimorphite $Zn_4Si_2O_7$ (OH) $2xH_2O$** found almost everywhere and often forms euhedral crystals. Massive or fine-grained aggregates of white hemimorphite is found in clusters of calcite-hemimorphite-barite-willemite composition.

**Willemite $Zn_2SiO_4$**, was detected in several samples in calcite-hemimorphite barite-willemite massive aggregates, where its content is less than 5% of its weight. It occurs as fine transparent, white, pale yellow or light brown to pale red crystals euhedral shape or as a reddish-brown nodules concretion in the cracks and voids.

**Smithsonite $ZnCO_3$** forms racemose and bundle aggregates among galenite and cerussite accumulations. Its secretions are found in cracks, voids and cavities in association with hypergenic zinc minerals. Smithsonite crystals are colored white, brown or gray. Aggregate of Smithsonite can reach several centimeters, sometimes they are covered with a film of oxides and hydroxides of manganese and iron.

**Zincite ZnO** occurs in the form of massive aggregates of granular grains, sometimes forms hexagonal crystals of orange or red color. Usually it is in association with hemimorphite and willemite.

**Sauconite $NaO_3Zn_3$ (Si, Al)$_4$$O_{10}$ (OH) $_2$ * $4H_2O$** belongs to the montmorillonite group and trioctahedral smectites with monoclinic syngony. Saukonite is associated with hemimorphite and clay minerals near barite ore bodies.

**B) Lead minerals** also constitute of a special group. Their formation occurs as a result of oxidation of galena.

**Anglesite $PbSO_4$** is formed by oxidation of galena and often develops along fissures in galena, where it can be present together with cerussite and barite. It is also found in the form of small prismatic crystals of pale yellow color with a size from 0.1 mm to more than 1 mm.

**Cerussite $PbCO_3$** is a product of the replacement of grains of galena and its mineral aggregates. Crystals of cerussite are colorless to white, and in some cases to black color due to impurities of oxides and hydroxides of iron and manganese. The size of the crystals varies from microscopic to more than 1 centimeter.

**Wulfenite $PbMoO_4$** occurs as a transparent yellow, orange or red colors tetragonal crystal form may also form aggregates of tabular or granular mass.

**Dekluazit Pb (Zn, Cu) $VO_4$ (OH)** represented crystals of different shapes, including - tabular, pyramidal and prismatic. The color of the crystals varies from black to dark green, olive green, light brown and light red with a strong metallic radiance. Its crystals are about 3 mm in size, but can reach more than 1 cm in deep zones.

**Vanadinite $Pb_5$ $(VO_4)_3Cl$** forms crystals in the form of small hexahedral prisms, sometimes hollow, measuring less than 0.1 mm to 1 mm, and having a bright brownish-orange color. Vanadinite is found in caverns and cracks in limestones in the zone of relatively deep oxidation.

**Pyromorphite $Pb_5$ $(PO_4)_3Cl$** is found in association with galena, cerussite, anglesite and calcite among oxidized ores. Its crystals form hexahedral, hollow and barrel-shaped aggregates. In addition, pyromorphite can form massive aggregates of grains or occur as crusts in the zones of oxidation of galena.

**Kotunit $PbCl_2$** - a rare mineral. It is a binary inorganic compound (lead chloride), which was found in the area of work in association with dolomite-galena as a result of electron microscopic studies. The kotunite is represented by transparent crystals of rhombic syngony, fills cracks and voids in dolomite samples.

**Iron oxides.** Ferric oxide minerals are found in the brecciation and fracturing zones, where they form fine-grained aggregates of reddish-brown color, composed of hematite $Fe_2O_3$, limonite FeOOH • ($Fe_2O_3$ • $nH_2O$) and goethite FeO (OH). Iron ore minerals fill, as a rule, cracks and form deposits on the surface of ore rocks.

**Manganese oxides** are also found in zones of fracturing and brecciation of near-ore rocks, where it is often associated with iron oxides (hematite, goethite, limonite). Their main mass is pyrolusite $MnO_2$, which forms black solid and dendritic-like deposits on the open surface of limestones and dolomites. It is associated with Hollandite Ba ($Mn_4$ +, $Mn_2$ +) $_8O_{16}$ and novelsite Ba ($Mn_4$ +, $Mn_3$ +) $_5O_{10}xH_2O$, which manifest themselves as thin needle crystals in the aggregate mass.

**2).Nonmetallic minerals**:

**Gypsum $CaSO_4$ * $2H_2O$ and anhydrite $CaSO_4$**. Gypsum by color can be white, bluish, grayish, less often reddish, pale brown or gray if it contains inclusions of other minerals. Anhydrite forms thick-plate, prismatic crystals or their aggregates, composed of continuous granular and six-column precipitates.

**Dolomite CaMg $(CO_3)_2$** is one of the most common minerals in the zones of peri-ore changes, where it occurs as inclusions and veins together with calcite, as well as fine and fine aggregates in limestones, giving them a granular structure and a vein-spotted texture .

**Celestine $SrSO_4$** is found in the form of isolated crystalline aggregates or as a secondary component in association with barite in veins.

Thus, the mineral composition of the ore mineralization of Wadi al-Masila is represented by a variety of minerals. The main minerals are barite and galena-sphalerite, which represent the hydrothermal stage of the formation of the deposit. A wide complex of secondary minerals is associated with processes of hypergenic transformation of the initial mineralization.

**Geochemical features of barite-polymetallic mineralization**. The study of trace elements in a barite-polymetallic mineralization Wadi Al-Masila is according to spectral and X-ray fluorescence analysis (Mattash et al, 2012;. Mattash, Al Haj 2014; Mattash, Al-Hajj et al, 2014;). Barite-polymetallic mineralization Wadi Al-Masila characterized by the constant presence of major elements (Si, AI, Ca, Na), associated with the relics of detrital matter surrounding rocks. Except barium, the main useful components are zinc (1-23%) and lead (1-20%). Wide range of chemical trace elements are associated to lead. The chemical composition of mineral samples galena was confirmed to contain elements such as: Se, Te, Cd, Ag, Zn, Co, Mn, Cr, Fe, Mg, Ca, Sr, Ba, Sb, Bi, Sn, Cu, Mo in prominent amounts . The veins are marked by the accumulation of oxides and hydroxides of iron and manganese.

## 4. Mineralogical and petrographic characterization of near-ore rocks and their alterations

The sedimentary cover of Wadi Al-Masila Basin presented the Jurassic, Cretaceous, Paleogene and Quaternary sediments, overlied on a fractured foundation of Proterozoic age (see Table 1).

**Lithological and petrographic characteristics of the sedimentary rocks of the Wadi Al-Masila Basin**. Lithological and petrographic studies of the sedimentary rocks of the Wadi al-Masila basin showed the following features of their structure (Al-Hajj et al., 2014).

**Upper Jurassic deposits. The Madbey formation** is composed of bituminous, foliaceous clay shales, marls, dolomites and limestones. Considering that mainly carbonate rocks enter the zone of influence of hydrothermal processes, we have considered only altered limestones and dolomites. The composition of the original rocks and the nature of their transformation in the Madby formation can be distinguished to: ferruginous limestones, dolomitized limestones, ferruginous dolomites.

**Formation of Neifa** is composed of lumpy-oolitic limestones. Limestone is 80% littered with organic residues, 20% cemented. Organic residues 0.1-0.5 mm in size are cemented with calcite cement. Limestone contains numerous (20-25%) inclusions of quartz crystals and aggregates, evenly distributed in the rock volume.

**Lower Cretaceous deposits. Formation Saar** is a productive stratum, to which the bulk of the mineralization is confined. It is composed of clay limestones and marls, sandstones with thin intercalations of limestones, reddish calcareous mudstones, siltstones, sandstones, gray shales with fossils and interlayers of dolomitized limestones. Carbonate rocks are mainly ore-bearing. Mineralization is associated with zones of fracturing and brecciation, the cracks are filled with hypogene aggregates of barite, galena, sphalerite and pyrite.

**Formation of Kishn** consists of a complex of terrigenous rocks, represented by sandstones, shales and conglomerates (below) and a complex of carbonate rocks (above), which is composed of limestones with interlayers of shales and sandstones.

Lower member. The conglomerate is calcareous, dark gray, dense, with a spotty texture due to the presence of large, rounded debris of calcareous and siliceous rocks of light gray, red and reddish color. The 65% conglomerate consists of fragments of sandstones and limestones, 35% - of cementitious material.

Upper member. Limestone organogenic, light gray with a yellowish tinge, dense, massive, with numerous inclusions of brachiopod shells. Limestone at 65-70% is composed of organic residues, 30-35% - cementing agent.

**Paleogene deposits. Formation Umm Er Raduma** is composed of organogenic and argillaceous limestones with interlayers of foliaceous shales. Limestones organogenic, light gray with a yellowish tinge, dense, massive, weakly cavernous, with rare calcite veins. The structure of the breed is biomorphic, the texture is massive, spotted areas due to uneven recrystallization.

**Volcanic rocks** are represented by olivine basalts. The structure of basalts is uneven granular, the texture is massive, patchy areas due to the presence of large grains of olivine. The rock consists of acicular crystals of basic plagioclases, 20% of pyroxene grains of irregular shape, 15% of isometric grains of olivine, around which there is a serpentine rim, partially replaced by iron hydroxide oxides.

**Wallrock alterations the host rocks**. Formation of barite-polymetallic mineralization in the basin of Wadi Al-Masila was accompanied by hydrothermal reforms of sedimentary rocks with powerful metasomatic zones formation. The most significant manifestation of the intensity of near ore metasomatic processes are dolomitization, silicification and iron ferrugination the host rocks.

**Dolomitization** developed in limestones in direct contact with the sheet-barite veins. Dolomitization and bedded zones presented lenticular bodies introduced in organogenic limestones. Sites of dolomitization creates confined streaks zones and blotches nesting galena-sphalerite mineralization. The process dolomitization was accompanied by leaching organic limestone and deposition of secondary calcite.

**Silicification** has irregular character. In some cases, silica uniformly impregnates the host rocks, in others - forms the concretions, crusts and druze in pre-existing cavities. All quartz crystals have a zonal structure due to mechanical admixtures. Such features of the structure of quartz indicate: 1) the mineral substances to individuals coming from all sides;

2) silica flow in porous limestone solution was pulsating with rhythmic character; 3) metasomatic process developed in already formed carbonate rocks.

**Ferrugination** is the most widespread in the near ore space barite-polymetallic veins. The pigmentation of sedimentary oxides, iron hydroxides can be traced up to 0.6 km to the sides and up the section of the veins. Due to the uniform distribution of ferrous minerals, rocks acquire relatively homogeneous dark brown color. Hydroxides of manganese are often associated with iron oxides minerals.

The distribution pattern of secondary hydrothermal-metasomatic limestone alteration allows to identify the following sequence changes. The beginning of overlay process, obviously, is organic limestone dolomitization. The next development is the silicification of host rocks. The last stage is ferrugination near-ore rocks.

## 5. Typomorphic signs barite mineralization

***Crystal chemical features of barite on the EPR data.*** This chapter provides crystal-chemical features of different types of barite barite-polymetallic ore bodies basin of Wadi Al-Masila (Al-Hajj, Khasanov et al., 2015). The electron paramagnetic resonance (EPR) method was selected as the main research method that allows to identify the subtle structural features of the minerals from the spectra of radical ions. The effectiveness of the EPR method used in barite study is based on two basic facts: 1) the formation of radical ions associated with the change in the charge state as a result of growth processes, or radiation damage; 2) The EPR is an ideal method for the detection and identification of these defects.

**EPR study results samples of various types of barite mineralization**. The research focused at barite mineralization samples, taken from the veins, bedded and altered host rocks containing inclusions of barite and ore minerals (Al-Hajj, Khasanov et al., 2015). Laboratory radioactive forcing of the sample to create universal small-sized X-ray source microfocal "XRS-50/50." As an internal standard, we used $I_E$ intensity of the EPR line of the ion $Cr^{3+}$ in $Al_2O_3$ crystal. The results of the studies are given below.

1) Residential barite with galena.

A) The sample (sample 2) is a vein of barite with galena and other ore minerals in the hydrothermally altered dolomite.In the hydrothermally altered dolomite, containing grains of white barite, inclusions of galena and cerussite, an EPR spectrum of SO3- (I) is observed in the radical region both in the initial rock and after its thermal annealing at 350 ° C: gxx = 2.0034; Gyy = 2.0024; Gzz = 1.9995.

Artificial irradiation with X-rays activates the "precenters" SO32- + e + = SO3- and we observe at once two types of ESR of ion radicals - SO3- (I) and SO3- (II) (gxx = 2.0076; gyy = 2.0022 ; Gzz = 1.9979) both in the original rock and after thermal annealing at 350 ° C. The center model is represented by the vacancy of one oxygen atom (O2 and O1, respectively for SO3- (I) and SO3- (II) centers) in a tetrahedron and the nearest barium atom. It should be noted that these centers have different annealing temperatures: at 140 ° C, the SO3- (II) center disappears, and at 400 ° C the SO3- (I) center disappears. After irradiation, the total intensity of SO3- (I) and SO3- (II) centers increased almost twice in the initial sample and decreased in the annealed sample. After thermal annealing, we saw lines of an additional $SO^2$-PC with parameters gxx = 2.0033; Gyy = 2.0126; Gzz = 2.0105, which is annealed upon irradiation with x-ray radiation. Thus, the EPR spectra in the radical region obtained in the initial sample and after annealing at 350 ° C indicate that barite has already been subjected to thermal transformations and has a stable structure.

B) The sample is an aggregate of radial-radiant barite crystals with large galenite inclusions up to 1-2 cm (sample 15). A similar pattern is observed for this sample. After irradiation of the initial and thermal-annealed 350 ° C rock, not only the formation of the SO3- (II) signal occurs, but also an increase in its intensity as the dose of irradiation is added.

2) Dolomite with inclusions and veins of calcite (sample 4). The rock is characterized by a brown color, fine-grained structure, vein-spotted texture, which is caused by the presence of inclusions and veins of calcite. In the region of radicals, there are no EPR spectra in the original rock. X-ray additional treatment of the rock activates SO3- in calcite, E 'in quartz, Rorg OB. In the dolomites, a more complex EPR spectrum of $Mn^2$ + is observed than in calcite. A measure of the relative salinity of the positions of $Ca^2$ + and $Mg^2$ + by impurity ions of $Mn^2$ + in the dolomite is the ratio $\alpha$ = 15 IMg / ICa, where IMg and ICa are the line intensities. The measure of salinity in sample 4-2 was $\alpha$ = 20 and is an indicator of the recrystallization and salinity of the basin. The indicator of barite is the EPR of ion radicals $SO^3$-. The absence of other paramagnetic centers in barite and EPR of Fe3 + and Mn2 + ions in the host rock is an indicator of the predominance of oxidation conditions. The thermal treatment of barite rock at 350 ° C does not change the number of precenters, which is possibly the result of recrystallization and thermal transformation of the rock. The trace concentration of paramagnetic centers is a consequence of the absence of strong radiation sources.

3) Mineral aggregates of zones of Wallrock alterations. The sample is represented by a brecciated vein material with barite, calcite and iron, manganese and zinc oxides. The mineral aggregate, which is a non-uniformly grained mass with large inclusions of barite, is taken from the oxidation zone of the barite vein. EPR spectra of $SO_3$- (I) indicate thermal stability at $350^0$C and similarity of genetic conditions of rock formation. Annealing 950 ° C revealed the presence of paramagnetic ions of manganese and iron in the newly formed barium oxides.

4) The stratiform type of barite (sample 17) is a homogeneous coarse-grained barite aggregate with shiny chips on the cleavage plane of white color (ex.17-1), as well as milk-white barite aggregates with bluish areas (sample 17-2) And white (17-3) colors. The large-crystalline aggregate of colorless barite has a homogeneous transparent structure (sample 17-1). The EPR spectra of this sample belong to the ion radicals SO2- and O- (I). In the coarse-grained aggregate of milky white barite, two inhomogeneities were investigated-arr. 17-2 from the gray-blue part and 17-3 from the milky-white part. The EPR spectra of samples 17-2 and 17-3 are represented by intense lines of SO2-, SO3- (I) and SO3- (II) ion radicals. It can be assumed that this aggregate of milky white barite is a homogeneous structure. A feature of vein (stratiform) barite is that neither in the initial rock sample nor after thermal treatment at 350 ° C EPR spectra are observed.

Results of radiation analysis of barite samples from different types of mineralization. To determine the natural radiation status of barite-polymetallic ore ores, gamma-spectrometric analysis was performed on Ra, Th, K (Al-Haj, Khasanov et al., 2015). The same samples of stratiform and vein barite were analyzed, containing rocks and aggregates selected from Wallrock alterations brecciation and oxidation zones. The results of the radiation analysis showed the presence of $^{226}Ra$ and $^{40}K$ radioactive isotopes in the samples under study, which are noted, first of all, in samples with vein barite and galena, and also rocks affected by hydrothermal processes. This indicates the presence of natural sources that have a radiative effect on the source ore. Taking into account that $^{226}Ra$ is formed as a result of radioactive decay of $^{238}U$, it can be assumed that the source of natural barite irradiation could be in the composition of deep solutions, which is indirectly indicated by the presence of hypogene galena PbS. As you know, lead is the final product of the decay of uranium. In unchanged enclosing limestones, radioactive elements are not noted (within the sensitivity of the method). They are also not fixed in stratiform barite, which indicates its formation in near-surface conditions at the initial stages of the process.

Features of the distribution of electron-paramagnetic centers in barites of various types and their typomorphism. As a result of the research, a number of interesting conclusions were obtained.

The study of stratiform barite showed that neither in the initial sample of the rock nor after thermal treatment at 350 ° C the EPR spectra were observed (weak significant). This may mean that when forming barite crystals in the vein, there were no sources of natural radioactivity or their influence was extremely insignificant. Due to the absence of defects in the crystal lattice, barite in stratiform veins is characterized by a more perfect crystal structure. The low concentration of the paramagnetic centers of the radical ion SO3- indicates the formation of barite with the participation of hydrothermal solutions.

EPR studies of barite samples showed that they are characterized by the presence in the crystal structure of a different number of paramagnetic centers, which allows them to be separated according to their genetic characteristics. Results of the research Khasanova RA With co-authors (1985) showed that barites from genetically different deposits and even from one deposit differ from each other both in intensity of the EPR spectrum of one or another ion radical, as well as in the ratio of the intensities of the lines of various ion radicals. Barite samples of various deposits are characterized by the presence of the radical ion SO3- and, as a rule, the intensity of its EPR spectrum line is small. In samples containing a greater number of different types of ion radicals, the intensity of the lines of the EPR spectra is usually higher. This dependence is characteristic, first of all, for barytes from the hydrothermal-sedimentary type deposit.

The results of EPR studies of samples of vein barites and barites in a number of conglomerates of the Wadi al-Masila deposit made it possible to specify the genetic type of barite ore occurrences. Table 3 shows the types of ion radicals observed in the barite studied (single and in the set), acting as a typomorphic feature for the corresponding genetic type of mineralization.

Table.3

The genetic type of mineralization by EPR data

| Number Sample | Name Sample | ion-radical type in barite | The genetic type of mineralization by EPR data ЭПР |
|---|---|---|---|
| 2 | Barite vein with galena | $SO_3^-$(I) | Hydrothermal-vein |
| 6 | Barite vein with galena | $SO_3^-$(I) | Hydrothermal-vein |
| 13 | Barite vein with galena | $SO_3$-(I) | Hydrothermal-vein |
| 15 | Barite vein with galena | $SO_3^-$(I), $SO_3^-$(II) | Hydrothermal-vein |
| 4 | Dolomite zone of near-ore | $SO_3^-$(I) | Hydrothermal-vein |
| 2032 | Brecciated zones near ore aggregates | $SO_3^-$(I) | hydrothermal metasomatic |
| 2033 | Brecciated zones near ore aggregates | $SO_3^-$(I) | hydrothermal metasomatic |
| 17a | Type stratiform barite | $SO_2^-$, $O^-$(I) | Hydrothermal - sedimentary |
| 17б | Type stratiform barite | $SO_2^-$,$SO_3^-$(I), $SO_3^-$(II), $O^-$(I), $O^-$(II) | Hydrothermal - sedimentary |

**Thermobarogeochemical characteristics of barite mineralization**. Nonmetallic minerals barite veins can be very informative to determine the characteristics of the formation, as their crystals contain relics of the primary gas-liquid fluid. Homogenization method were used to investigate fluid inclusions in barite, calcite and quartz (Mattash, Al-Hajj et al, 2014; Mattash, Al-Hajj et al, 2015). Gas-liquid inclusions that are conserved in the voids of minerals carry out information about the temperature conditions of their formation. According to the order, the inclusions selection are classified into primary, formed in the mineral in the process of crystallization, and the secondary, which arise in the mineral after its complete cessation of growth and are localized in cracks or other defects in the body cavities of the crystal. Secondary inclusions can not be used to restore the crystal growth conditions. In phase composition they are divided into: 1) single-phase liquid; 2) two-phase gas-liquid; 3) solid-liquid inclusions.

In order to determine the characteristics of the formation of ore mineralization, fluid inclusions (gas-liquid inclusions) in quartz, calcite and barite were investigated. We found the presence of primary and secondary inclusions, which are divided by the phase composition: 1) single-phase liquid; 2) two-phase gas-liquid; the result of the study revealed that the homogenisation of primary inclusions in quartz occurs mainly in the liquid phase in the temperature range 305 - 312 ° C; in calcite occurred in the two-phase (gas-liquid), a temperature in the range 174-210 ° C; in barite occurred also in two-phase (gas-liquid) in the temperature range of 280 - 195 ° C.

6. Conditions for the formation of barite-polymetallic mineralization

**Mineral associations and stages of mineralization**. Barite-polymetallic mineralization at Wadi al-mass timed to handful Mesozoic sediments in the field of Paleogenic formations. It is localized in carbonate rock formations Saar (K1b-K1v1) which is the main productive horizon in the below of cretaceous period. On the basis of textural and structural analysis of ores (relationships between minerals) and thermometric studies, we classify it in 5 paragenetic mineral association:

1. Calcite - (dolomite) - (quartz) - (pyrite).
2. Barite 1 - calcite - (quartz) - (dolomite).
3. Barite 2 - calcite - galena - sphalerite - (dolomite) - (quartz)
4. Barite 3 - calcite - galena - sphalerite - (dolomite) - (quartz).
5. cerussite - gemmimorfit - gidroargetit - pyrolusite.

Thus, the formation of mineralization occur in stages over a long time, which explains the diversity of the mineralogical composition and structural - textural features of ores. Stages of mineralization with the crystallization temperature intervals of main minerals, which established by termobarogeochemical studies includes two stages - hydrothermal and supergene.

***I. Hydrothermal stage.*** Hydrothermal activity was continuously intermittent (pulsating) nature. Composition of hydrothermal fluids and their temperatures are changing over time, which served as the basis for the separation of hydrothermal stage into four stages:

1) premineral,
2) ore I,
3) ore II ,
4) post-ore.

***II. Supergene stage.*** This is the final stage. During its formation, occurred a wide range of secondary minerals due to changes in the conditions of ore formation environment ( increase of oxidative capacity, Eh and pH of the environment to slightly alkaline). On supergene stage, by dissolving the ore minerals formed anglesite, tsinkozit sulphate, vanadium, and others.

In general, supergene (oxidation) stage can be characterized as a stage of secondary enrichment of polymetallic ores.

## CONCLUSION

1. Barite-polymetallic mineralization in the basin of Wadi Al-Masila has a complex mineral composition. Minerals are presented as sulphate, carbonate, sulfide, oxide and silicate compounds, the formation of which occurred as a result of crystallization from solutions and metasomatic transformations enclosing sedimentary rocks during hydrothermal activity and supergene.

2. Barite of various types are characterized by crystal-chemical features associated with conditions of their formation. Typomorphism barite due to the presence of the mineral structure of the paramagnetic defect centers ($SO_4^{3-}$, $SO_3^-$, $O^-$, $SO_4^-$, $SO_2^-$, etc.) arising from the isomorphic replacements, artificial and natural radiation exposure. The last of which has a profound nature and associated with the presence of hydrothermal hypogenic solutions components containing radioactive decay products of uranium. Barite typomorphism shows its genesis and history of radiation.

3. The origin of the mineralization is associated with tectonic activity and accompanied by hydrothermal activity during the formation of Red Sea rift (Gulf of Aden) and penetration along the faults of hydrothermal solutions. The complexity and variety of the mineral composition of the multistage mineralization is due to its formation. Stages of mineralization with the crystallization temperature intervals of main minerals, which established by termobarogeochemical studies includes two stages - hydrothermal and supergene. Formation of the main mineral reflects the pulsating nature of the mineralization of hydrothermal activity during the formation of Red Sea rift. The temperature range of formation of hydrothermal mineralization according to thermometry is 312 - 174 ° C.

The results can be used to determine the conditions for the formation of complex barite-polymetallic ores, as well as their forecasting and research.

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