

Mineralogy of gold-telluride-sulfide ores of the Kokkiya deposit, Kazakhstan

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Abstract

Purpose. To establish the mineral-forming sequence and clarify the features of gold-telluride-sulfide mineralization at the Kokkiya deposit based on the study of mineral assemblages, typomorphic characteristics of ore minerals, modes of occurrence of native gold and tellurides, and their spatial and paragenetic relationships.

Methods. A total of 120 ore and host-rock samples collected from drill core were studied. The analytical methods included optical microscopy in reflected and transmitted light, scanning electron microscopy, electron-probe microanalysis, EDS/WDS analysis, and EDS mapping. Gold fineness and composition were additionally compared with depth, pyrite generations, structural and textural characteristics of the ores, and hypogene and supergene mineral assemblages.

Findings. Two main stages of mineralization were distinguished: hypogene and supergene. Four successive stages were identified within the hypogene stage: pre-ore hydrothermal-metasomatic, early pyrite, main telluride-polymetallic, and late pyrite-polymetallic. Pyrite is the principal ore mineral and is represented by several generations differing in morphology and paragenesis. Native gold is associated with pyrite, quartz, sericite, galena, and tellurides. The later stages are characterized by calaverite, petzite, altaite, tsumoite, native tellurium, and Bi-bearing minerals. Gold fineness in intergrowths with altaite and calaverite ranges from 944-977‰, whereas in oxidized ores it ranges from 634-820‰. EDS mapping confirmed the close spatial association of micron-scale gold inclusions with telluride phases. The most intense mineralization is confined to the inner, most strongly altered parts of the metasomatic zonation.

Originality. The mineralogical-genetic model of the Kokkiya deposit has been refined by linking pyrite generations, gold fineness, telluride mineralization, and the sequence of ore-forming stages. The distribution of gold and tellurides is shown to reflect the multistage evolution of the hydrothermal system and subsequent supergene alteration.

Practical implications. Sericitolites, Te- and Bi-bearing minerals, characteristics of pyrite generations, and gold-telluride associations can be used as mineralogical exploration criteria for evaluating prospective zones and the potential continuation of productive mineralization at depth.

Keywords: deposit genesis; mineralization; native gold; tellurides; sulfides; metasomatites

1. Introduction

Studies of ore-forming processes show that the formation of many gold deposits is closely related to hydrothermal-metasomatic processes and the multistage evolution of ore-forming systems [1]-[3]. Gold-telluride deposits are of particular interest because they are characterized by complex paragenetic relationships between native gold, sulfides, tellurides, and other rare ore minerals. Similar mineral assemblages have been identified, in particular, within the Bereznjakovskoe ore field, at the Kairagach and Kochbulak deposits, and in other gold-telluride hydrothermal systems [4]-[9].

Modern studies of mineral deposits increasingly rely on an integrated analysis of geological structure, structural and tectonic controls, and the spatial variability of ore systems. Considerable attention is paid to assessing the geodynamic

state of the geological environment, studying rock-mass fracturing, constructing three-dimensional models of geological objects, and applying geophysical and remote sensing methods to identify prospective areas [10], [11]. Current developments in this field include methods of geodynamic forecasting, fracture-system analysis, gravity modelling of bodies with different geometries, geoinformation modelling, and the integrated use of geological and satellite data in exploration targeting [12]-[15]. Studies of ore deposits in Kazakhstan also increasingly combine lithophysical and geophysical data to refine the structure of productive strata, identify structural heterogeneity, and delineate zones of tectonic and mining-induced disturbance [16], [17].

Another important research direction is the assessment of spatial ore heterogeneity and the distribution of valuable

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components within deposits [18]. Studies in this field focus on substantiating ore-grade averaging, accounting for variations in metal content and the degree of reserve preparedness, and improving mine planning with consideration of mineral raw material quality [19]-[22]. The mineralogical composition and structural characteristics of ores are important not only from a genetic perspective but also in practical terms, since they can significantly affect the physical and technological properties of productive horizons and the selection of mining parameters [23], [24].

For gold deposits, these issues are closely related to the modes of gold occurrence and the technological properties of the ores, because the mineralogical composition and degree of gold dispersion can substantially affect subsequent metal recovery [25]. Accordingly, a separate line of research focuses on improving gold leaching efficiency and the processing of complex gold-bearing sulfide concentrates [26], [27].

Along with the geological and technological study of ores, quantitative characterization of the dispersion and particle size of the material under investigation is becoming increasingly important. Methods for determining particle-size distribution make it possible to characterize the heterogeneity of dispersed systems in greater detail and can complement the mineralogical and technological assessment of raw materials [28]. At the same time, modern studies of gold-mining areas increasingly include geochemical and geoenvironmental assessments of the impacts of deposit development, including analysis of the spatial distribution of heavy metals and changes in the physicochemical properties of environmental components in gold-mining areas [29], [30].

The modes of gold occurrence and its relationships with tellurium and bismuth are important for reconstructing the conditions and sequence of ore formation. Tellurides of gold, silver, lead, and bismuth may form at different stages of hydrothermal system evolution, while their spatial and structural relationships with pyrite and native gold reflect changes in the physicochemical parameters of the mineral-forming fluid.

The Kokkiya deposit is located within the Kyrgyz-Terskey structural-formational zone and belongs to the gold-metasomatic type of deposits. Previous micromineralogical studies of gold-bearing metasomatites in this area revealed a complex ore mineral assemblage and the presence of finely dispersed native gold associated with sulfides and rare ore minerals [31]. Of particular interest is the occurrence of Te- and Bi-bearing phases closely associated with microscopic gold, as such assemblages may reflect the multistage formation of gold mineralization.

At the Kokkiya deposit, gold occurs predominantly as fine and micron-scale grains and is closely associated with pyrite, other sulfides, and tellurides. These modes of occurrence make direct identification of gold difficult and require an integrated study of the morphology, composition, and paragenetic relationships of the ore minerals. Particular importance is therefore attached to distinguishing different generations of pyrite and establishing the position of native gold and tellurides within the mineral-forming sequence.

The study of the typomorphic characteristics of native gold is important for reconstructing the formation conditions of gold deposits. Previous syntheses of mineralogical and geological data from different types of gold mineralization have shown that the morphology, composition, internal structure, and mineral associations of native gold can be used as

indicators of its genesis and ore-forming conditions [10]. The typomorphic features of gold reflect the stages of mineral formation, changes in mineral assemblages, and variations in the physicochemical conditions of ore formation at different levels of the ore-forming system [32].

The formation of gold mineralization is associated with the migration of hydrothermal fluids, their cooling, and interaction with the host rocks. Changes in temperature, pressure, fluid composition, and redox conditions may destabilize dissolved gold complexes and trigger the precipitation of noble and chalcophile elements [33]-[35]. In gold-telluride systems, these processes are accompanied by the formation of complex Au-Ag-Te-Bi-bearing mineral assemblages, whose composition and sequence of formation provide important indicators of hydrothermal system evolution [5]-[7], [9].

Despite the available mineralogical data on the Kokkiya deposit, the sequence of formation of the main ore assemblages, the relationships between different pyrite generations and native gold and tellurides, and the distribution of micron-scale Au- and Te-bearing phases require further clarification. Establishing these relationships is important both for reconstructing the genetic model of the deposit and for assessing the potential continuation of productive gold-telluride mineralization at depth.

The purpose of this study is to determine the mineral-forming sequence and the features of gold-telluride-sulfide mineralization at the Kokkiya deposit based on the study of mineral assemblages, typomorphic characteristics of the main ore minerals, modes of occurrence of native gold and tellurides, and their spatial and paragenetic relationships.

2. Study area

The Kokkiya deposit is located within the Kyrgyz-Terskey structural-formational zone, which comprises rocks of different ages ranging from the Lower Proterozoic to the Cenozoic. The lower part of the stratigraphic succession consists of metamorphosed Proterozoic rocks. The Paleozoic is represented by Ordovician terrigenous and volcanic complexes, whereas the Cenozoic comprises a complete stratigraphic succession, including Quaternary deposits.

Magmatism in the region is multiphase and dominated by Paleozoic intrusions. Several magmatic complexes are distinguished: the Late Cambrian-Early Ordovician and Middle Ordovician complexes, represented by mafic, intermediate, and felsic intrusions; the Late Ordovician-Silurian complex, comprising gabbroids, syenites, and subalkaline granitoids formed during several stages; and the Late Devonian complex, represented by subvolcanic bodies and the Merke granitoid complex. The region is characterized by extensive intrusive activity and a close relationship between magmatism and sedimentary associations [36].

The Kyrgyz-Terskey structural-formational zone extends across the southern part of Central Kazakhstan and includes formations developed under both oceanic and continental collisional settings. It occupies the southern part of the Central Kazakhstan segment of the Central Asian Orogenic Belt, an area that underwent multiple stages of tectonic and magmatic evolution. Thus, the tectono-magmatic evolution of the region reflects a complex, multistage geodynamic history involving collisional, subduction-related, and subsequent post-collisional processes, which accounts for the high metallogenic potential of the area [37].

This zone remains relatively poorly studied but is considered highly prospective for various mineral resources, including gold (Au), silver (Ag), tungsten (W), antimony (Sb), mercury (Hg), and base metals [38]. Early and Middle Paleozoic intrusions are widespread within the zone, particularly those of Late Devonian age, together with their volcanic equivalents. These magmatic rocks are associated with precious-metal mineralization, which commonly shows a pronounced tellurium-bismuth specialization.

The present study focuses on gold-metasomatic mineralization of the gold-quartz-propylite formation. Occurrences of this formation are developed on the northern slopes of the Kyrgyz Range (Taldybulak ore field) and directly along the sides of the Karakystak Valley, where rocks of the Devonian volcano-plutonic belt are exposed. Zones and fields of hydrothermally metasomatized rocks are superimposed on the volcano-plutonic complexes. Quartz-sericite metasomatites host a number of gold occurrences, including Taldybulak “Zolotoy”, Kokkiya, Yuzhnoye, Osenneye, Verkhniy Sargy-bai, and others. Their spatial distribution is controlled by tectonic structures and small intrusions of syenites, syenodiorites, and monzogranodiorites and generally shows a linear-nodal pattern. Among these occurrences, the Kokkiya deposit is of particular interest. It is composed of lavas and lava breccias of the Lower-Middle Devonian Aksu subvolcanic complex and stock-like syenite bodies of the Middle Devonian intrusive complex.

The geological position of the deposit is controlled by its location in the roof zone of a granodiorite massif belonging to the Upper Devonian intrusive complex. Stratified units are represented by terrigenous and volcanic rocks of the Aksai Formation (D1-2ak), exposed on the western flank of the area, as well as felsic crystallo-vitroclastic tuffs and conglomerates of the Taldysu Formation (D3ts), which occupy most of the central part of the study area.

Tectonically, the study area lies within the Kyrgyz-Terskey structural-formational zone. Within the investigated area, the eastern part of this zone is composed of a volcano-plutonic complex belonging to an independent Devonian volcano-plutonic belt [36], [39]-[41].

Faults play an important role in the structural development of the Kokkiya deposit. Within the study area, they are subdivided into major and secondary faults. The main E-W-trending structure is the North Kyrgyz fault, or deep-seated fault zone, which bounds the Kyrgyz Range mountain system to the north. The fault extends for hundreds of kilometres. To the west, it joins the Main Karatau fault, whereas to the east it continues along the southern slopes of the Trans-Ili Alatau, where it splits into several subparallel fault zones (Fig. 1).

Fluid migration along faults resulted in substantial changes in the chemical composition of the rocks within individual zones and led to the development of metasomatic zonation. At the Kokkiya deposit, the elevated parts of the terrain are composed of secondary quartzites underlain by propylitized rocks (Fig. 2). The sericite facies is the most widespread and best developed. It is overprinted by metasomatic and vein silicification, chloritization, and carbonatization. Quartz veins contain chlorite, Fe-bearing carbonate, and dolomite and host polymetallic mineralization associated with gold. This spatial association indicates that fault-controlled fluid pathways played a key role in localizing both hydrothermal alteration and ore mineralization.

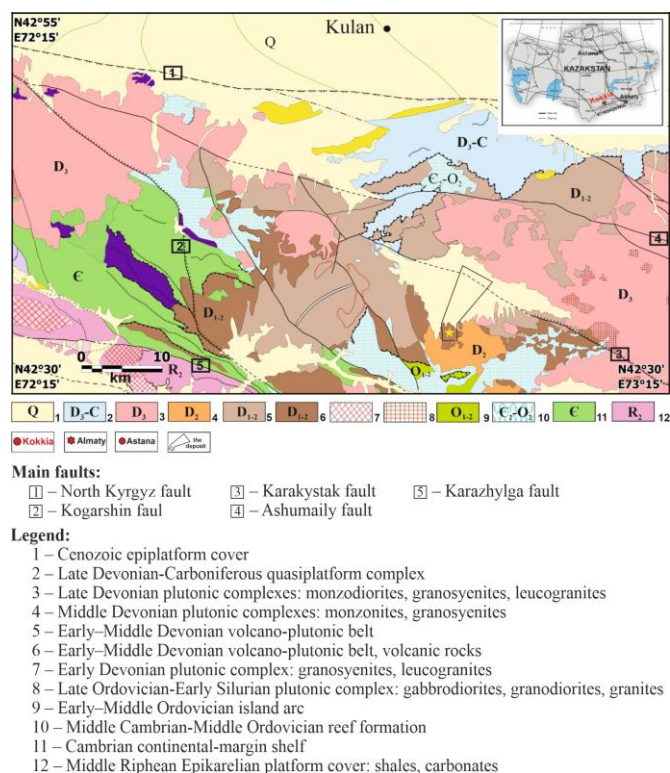


Figure 1. Geological map of the western part of the Kyrgyz Range

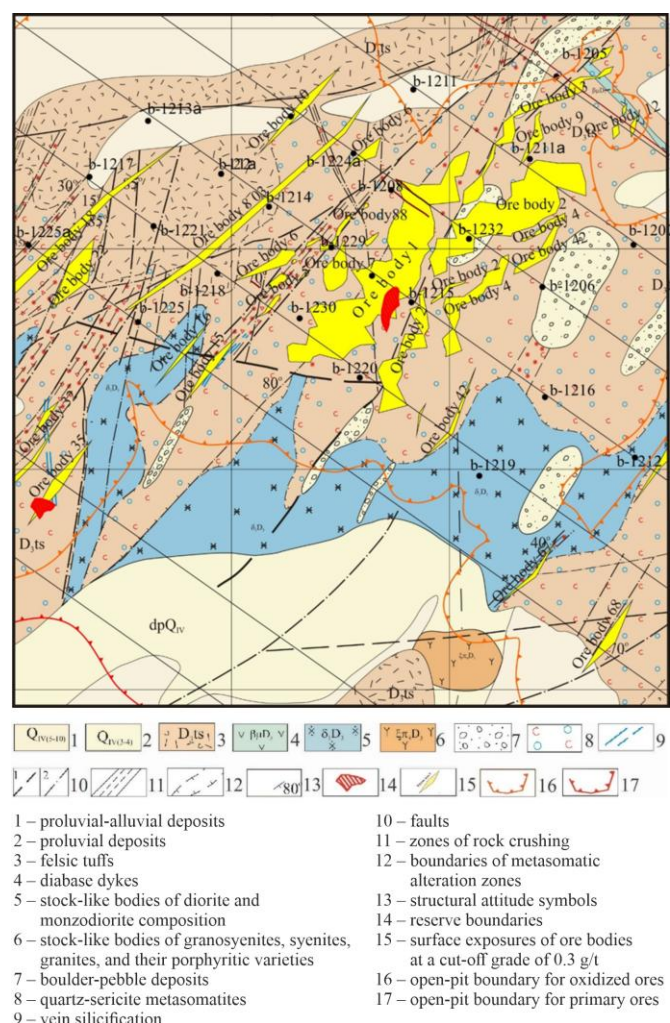


Figure 2. Schematic geological map of the Kokkiya deposit (Loparev S.V., 2013)

According to petrochemical analyses carried out to identify the mineral assemblages at different levels, the following zonally arranged secondary quartzite facies are distinguished from the periphery toward the centre [42]–[44] (Fig. 3):

- 1) propylitic alteration zone, represented by strongly chloritized, sericitized, albitized, K-feldspathized, carbonatized, and pyritized tuffs, conglomerates, and intrusive rocks;
- 2) kaolinite facies;
- 3) sericite facies;
- 4) diaspore facies;
- 5) monoquartz facies.

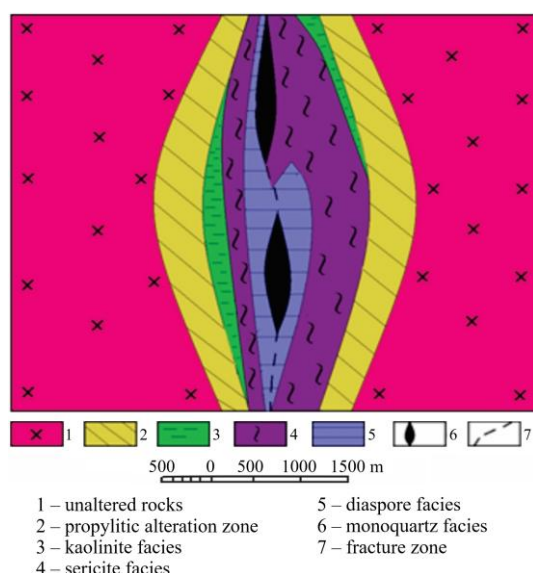


Figure 3. Schematic cross-section of metasomatic zonation at the Kokkiya deposit

Within the vertical metasomatic column of the Kokkiya ore field, pyrite-quartz-sericite altered rocks with varying degrees of gold mineralization are distinguished. Sericite-pyrite rocks (sericitolites) with higher gold contents were identified microscopically and may serve as a valuable exploration criterion. Refining the metasomatic zonation is important for identifying fluid migration pathways and, consequently, the most probable sites of ore mineralization. Ore bodies are generally localized in the axial parts of these metasomatic zones, which formed under weakly acidic conditions.

Gold, silver, and polymetallic mineralization is confined to a field of hydrothermally metasomatized rocks. The altered rocks are represented by bodies of secondary quartzites and propylites. Their distribution is controlled by stock-like and dyke-like intrusions of syenitic and monzodioritic composition belonging to the Middle Devonian intrusive complex.

The formation of secondary quartzites is related to metasomatic alteration by highly acidic fluids of polygenetic origin. In the inner zones of alteration, where fluid acidity was highest, all minerals except quartz were completely dissolved. As the fluids interacted with the host rocks, their acidity decreased, as indicated by the transition from monoquartz zones to quartz-sericite and subsequently quartz-clay assemblages. At the same time, the concentration of alumina in the fluids decreased, accompanied by intensive precipitation of high-alumina minerals. Filtration of highly acidic fluids through the rocks and their interaction with the host material resulted in the formation of monoquartz bodies in the core zones and high-alumina minerals around them [45].

The principal ore-hosting rock is a pyrophyllite-bearing sericite-quartz metasomatite, presumably formed by replacement of plagioclase porphyrite. The ores are dominated by quartz, sericite, and pyrite represented by several generations. Andalusite, alunite, corundum, diaspore, and pyrophyllite occur in minor amounts. Accessory and subordinate minerals include hematite, rutile, topaz, zuniyite, fluorite, and tourmaline.

Based on the relationships between andalusite and sericite, these minerals formed during the final stages of secondary quartzite development as temperature decreased. The widespread occurrence of andalusite in the metasomatites indicates a relatively shallow level of formation, while the low mineral-forming temperature suggests a low degree of erosion of the ore occurrence and the possibility that mineralization continues at depth. Judging from the described mineral assemblages of the secondary quartzites, the outer sericite facies is predominant at the Kokkiya deposit. Minerals characteristic of the inner zones occur as relics of the diaspore facies and only rarely form separate bodies.

The sequential development of secondary-quartzite mineral facies within the study area was probably disrupted by the cessation of gas and fluid supply or by changes in fluid acidity. This resulted in the absence of several facies typical of the secondary quartzite formation in Kazakhstan, including the corundum-andalusite, alunite, and pyrophyllite facies. With the exception of the sericite facies, the identified facies are poorly developed, discontinuous, and frequently overprint one another.

The highest gold contents in the metasomatites occur in the inner and core parts of the metasomatic column, that is, within the most intensely altered zones. The more intense the metasomatic alteration of the rocks, the richer the mineralization; an increase in the thickness of metasomatic alteration is accompanied by an increase in the thickness of the ore zones.

Weakly altered rocks in the near-ore environment form more extensive bodies characterized by low gold contents. The metasomatites of the ore field are ore-controlling formations, among which sericitolites represent a reliable exploration criterion for economically significant gold concentrations.

3. Methods

For comprehensive mineralogical-geochemical and micro-mineralogical investigations, 120 samples of ores and host rocks were collected from drill core from the Kokkiya deposit. The study was aimed at determining the mineral composition, mineral-forming sequence, typomorphic characteristics of the main ore minerals, modes of occurrence of native gold and tellurides, and the nature of their paragenetic relationships.

Polished surfaces were examined by optical and scanning electron microscopy. Optical studies were carried out using a Carl Zeiss Axio Scope A1 microscope in reflected and transmitted light at the innovative laboratory of Satbayev University (Almaty, Kazakhstan). Optical microscopy was used to study the mineral composition of the ores, their structural and textural features, the sequence of mineral formation, and the principal mineral assemblages. During the study of typomorphic features of ore minerals and native gold, their mineral associations, grain sizes and morphologies, and internal structural characteristics were determined.

Structural-analytical and microchemical investigations were performed using a JEOL JXA-8230 electron microprobe analyser (Tokyo, Japan). Micrographs were obtained mainly in backscattered-electron mode (BSE/COMPO),

while microanalytical data were processed using the built-in EPMA software. The analyses were carried out at the laboratory of the Institute of Metallurgy and Ore Beneficiation (Almaty, Kazakhstan). The accelerating voltage was 20 kV; the electron-beam current did not exceed approximately 3.5 nA for energy-dispersive spectroscopy (EDS) and 20 nA for wavelength-dispersive spectroscopy (WDS).

Qualitative analysis of ore minerals was performed using a Tescan Vega LMU scanning electron microscope equipped with INCA Energy 450 and INCA Wave 700 systems. The chemical composition of ore and vein minerals was additionally studied at Adam Mickiewicz University (Poland) using an S-3700N scanning electron microscope equipped with an EDS system. Quantitative microelement analysis of minerals was carried out at the Institute of Geological Sciences in Warsaw (Poland) using a CAMECA SX-100 electron microprobe analyser equipped with five wavelength-dispersive spectrometers and an energy-dispersive X-ray detector. Typical analytical conditions were 15-20 kV and a beam current of 20-30 nA. The instrument provided a spatial resolution of $\leq 1 \mu\text{m}$. Additional electron-probe microanalysis of Bi-bearing phases in iron hydroxides was performed using a Superprobe 733 microanalyser.

EDS mapping was applied to determine the spatial distribution of selected elements and to localize micron-scale inclusions of gold and tellurium. This made it possible to clarify the spatial relationships between native gold, tellurides, and sulfide minerals. Elemental maps were interpreted with BSE images and microanalysis data to identify microinclusions, establish relationships among native gold, tellurides, and sulfide minerals, and refine their paragenesis.

Additional analyses were carried out at the Mineral Resources and Environmental Research Center of Southern Federal University using scanning electron microscopy and X-ray fluorescence microanalysis. Chemical analyses of selected samples were also performed at AcmeLab (Canada).

To assess variations in gold composition through the vertical section of the deposit, gold content and fineness were analysed in ordinary ore samples collected from different depths and erosion levels of the ore bodies. When evaluating the relationships between gold content, fineness, and depth, results with anomalously high gold contents were excluded. The obtained data were compared with mineral assemblages, pyrite generations, and the characteristics of hypogene and supergene mineralization.

4. Results

4.1. Mineral-forming sequence and main mineral assemblages

The quartz content in sericitolites generally does not exceed 30-40%, whereas in quartz-sericite altered rocks it typically ranges from 40 to 70%, depending on the intensity and stage of alteration. Chlorite-quartz-sericite metasomatites are considerably less widespread. The highest concentrations of native gold occur in sericitolites.

Mineralization at the deposit comprises two main stages – hypogene and supergene. Within the hypogene stage, microscopic examination of rock and ore samples collected from drill core allowed several successive stages of mineral formation to be distinguished, as summarized in Table 1.

Table 1. Main mineral assemblages and mineral-forming sequence at the Kokkiya deposit

Stage	Assemblage	Minerals	
		Ore	Gangue
Pre-ore (hydrothermal alteration stage)	Quartz-sericite	Pyrite I, pyrite II	Quartz, chlorite, sericite, muscovite, zunyite, diaspore, pyrophyllite, kaolinite
Pyrite (early ore stage)	Gold-pyrite-quartz	Pyrite III, gold, arsenopyrite, bismuthinite, pyrrhotite, cassiterite, magnetite, hematite, molybdenite	Chlorite, sericite, diaspore, pyrophyllite, zunyite
Telluride-polymetallic (main ore stage)	Gold-telluride-pyrite	Pyrite III, gold, chalcopyrite, pyrrhotite, arsenopyrite, magnetite, tetrahedrite, tennantite, rutile, ilmenite, cassiterite, calaverite, tsumoite, petzite, altaite, tellurobismuthite, native tellurium	Chlorite, sericite, calcite, diaspore, sphene
Pyrite-polymetallic (late ore stage)	Gold-sphalerite-galena	Pyrite IV, chalcopyrite, sphalerite, galena, tetrahedrite, tennantite, goldfieldite, covellite, magnetite, hematite	Chlorite, sericite, calcite

4.1.1. Pre-ore stage

The pre-ore stage represents a stage of hydrothermal alteration characterized by the development of quartz-sericite and sericite-quartz metasomatites. The quartz-sericite assemblage is widespread throughout the deposit as microveinlets. Their gold content is very low; they occur mainly within weakly altered rocks of the outer facies, which are often genetically associated with gold-rich ore shoots and bonanzas.

Zones of gold mineralization tend to occur within the inner metasomatic facies composed of quartz, sericite, muscovite, zunyite, actinolite, tourmaline, diaspore, and minerals of the montmorillonite and kaolinite groups. The sericite-quartz facies, corresponding to the final stage of silicification, is the most fully and widely developed. It is represented by whitish rocks, locally with a greenish tint due to superimposed chloritization, and stained at the surface by iron hydroxides (Fig. 4).

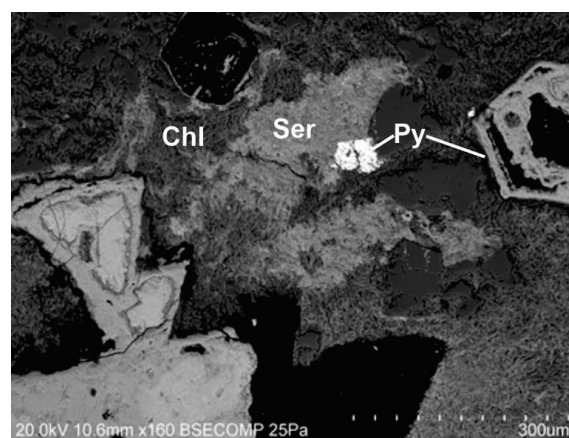


Figure 4. SEM-BSE micrographs of pyrite, sericite, and chlorite from the oxidation zone

Analyses of oxidized ores from the Kokkiya deposit showed that the fineness of gold enclosed in iron hydroxides at depths of 9-10 and 20-22 m ranges from relatively low to medium and moderately high values (634-820‰). Although high-fineness gold was not identified in the oxidation zone of the studied deposit, gold fineness tends to increase with depth, which may indicate insufficient development of the oxidation zone.

The fineness of gold intergrown with tellurides, including altaite and calaverite located between pyrite grains, ranges from 944 to 977‰. In galena and pyrite veinlets at shallow depths, the fineness decreases to 810‰. The decrease in the overall amount of gold in later assemblages may have resulted from fluid neutralization during interaction with the host rocks.

4.1.2. Pyrite, or early ore stage

Ore mineralization occurs as disseminations ranging from sparse to dense within quartz-sericite metasomatites. Sericite quartzites are overprinted by microveinlet silicification, chloritization, and carbonatization. The main ore mineral is pyrite, typically with pentagonal dodecahedral morphology and less commonly cubic forms. Bismuthinite, chalcopyrite, pyrrhotite, scheelite, wolframite, and magnetite occur in minor amounts.

In the near-surface zone, limonite develops after pyrite and commonly shows a colloform texture. Rare dust-like and irregular veinlet-like occurrences of native gold and silver are observed within the limonite. Mineralization of the pyrite stage is widespread throughout the Kokkiya deposit.

4.1.3. Telluride-polymetallic, or main ore stage

This stage is represented by tellurides of gold, silver, and lead, as well as native tellurium. At depths of 140-143 m, pyrite III is intensely corroded and becomes porous, while native gold, closely associated with gold, silver, and lead tellurides, fills its pores and fractures. Native tellurium and tellurides of gold (calaverite), bismuth (tsumoite), silver and gold (petzite), and lead (altaite) occur as disseminations and veinlet-like inclusions in fahlores (goldfieldite) and are associated with later vein quartz. Selenium is also present as an isomorphic impurity in galena, tsumoite, and bismuthinite.

4.1.4. Pyrite-polymetallic stage

Galena containing enclosed gold occurs as thin veinlets between grains of aggregate pyrite IV. This gold is of moderately high fineness. The silver content of native gold enclosed in late galena veinlets within aggregate pyrite IV systematically increases, which is characteristic of many gold deposits.

4.2. Typomorphic characteristics of the main ore minerals and native gold

Pyrite is the principal ore mineral of the deposit, whereas native gold is the main economically valuable component of the ores. Subordinate and rare ore minerals define the geochemical specificity of ore formation at the deposit. Among the rare minerals, gold telluride (calaverite), bismuth telluride (tsumoite), and gold-silver telluride (petzite) are of particular importance.

Pyrite in the metasomatites occurs as disseminations ranging from sparse to dense, as well as in nests up to 1 cm in size. In the near-surface parts of the deposit, it is oxidized and commonly occurs as pseudomorphs.

Several generations of pyrite have been distinguished.

Pyrite I has a cubic morphology and occurs as fine disseminations, predominantly 0.01-0.05 mm in size and locally up to 0.1 mm, within dark greenish chlorite-quartz-sericite metasomatite. It is associated with chlorite and sericite (Fig. 5a).

Pyrite II is much less abundant and occurs as fine-grained veinlet-chain aggregates. It probably develops after unstable marcasite and, through recrystallization, transforms into pentagonal dodecahedral, octahedral, and, less commonly, cubic pyrite III (Fig. 5c).

Pyrite III occurs as pentagonal dodecahedral, octahedral, and cubic crystals forming uneven disseminations and contains fine gold inclusions. In sericitolites, it is intensely corroded, and grain sizes reach 0.4 mm. At depths of 140-143 m, the degree of corrosion increases, pyrite becomes porous, and its pores and fractures are filled with native gold closely associated with gold, silver, and lead tellurides.

Pyrite IV is coarser-grained than pyrite I and pyrite II. Its grain size ranges from 0.1-0.3 mm, and it forms intergrowths and aggregate accumulations within the metasomatite. Aggregate pyrite is cut by fractures along which later sphalerite, galena, and chalcopyrite developed (Fig. 5b, d). Tellurium minerals associated with gold also occur in the intergranular spaces of aggregate pyrite, whereas chalcopyrite, galena, pyrrhotite, fahlores (tetrahedrite, tennantite, and goldfieldite), arsenopyrite, covellite, bismuthinite, cassiterite, magnetite, and hematite are less common.

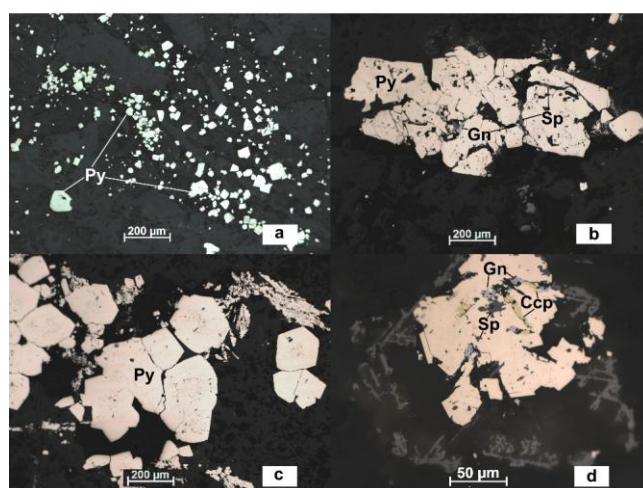


Figure 5. Microscopic images of different pyrite generations from the Kokkiya deposit: (a) fine-grained cubic pyrite I in chlorite and sericite; (b) aggregate pyrite IV (Py), with galena (Gn), chalcopyrite (Ccp), and sphalerite (Sp) in the intergranular spaces; (c) veinlet-like pyrite II associated with pentagonal dodecahedral pyrite III; (d) chalcopyrite (Ccp), sphalerite (Sp), and galena (Gn) veinlets filling voids between pyrite IV (Py) crystals

Galena occurs as isolated inclusions, including fine inclusions in sphalerite, develops along fractures in aggregate pyrite, and rarely forms intergrowths with chalcopyrite (Fig. 6a).

Accumulations of submicron gold particles occur at the contacts with late sulfide veins, and their abundance decreases with increasing distance from the veins. This feature, together with the presence of fractures in sulfide grains, facilitates the identification of dispersed gold during microscopic examination. Galena inclusions range in size from 0.03 to 0.05-0.15 mm. Late galena develops along fractures in aggregate pyrite and contains gold mineralization (Fig. 6b).

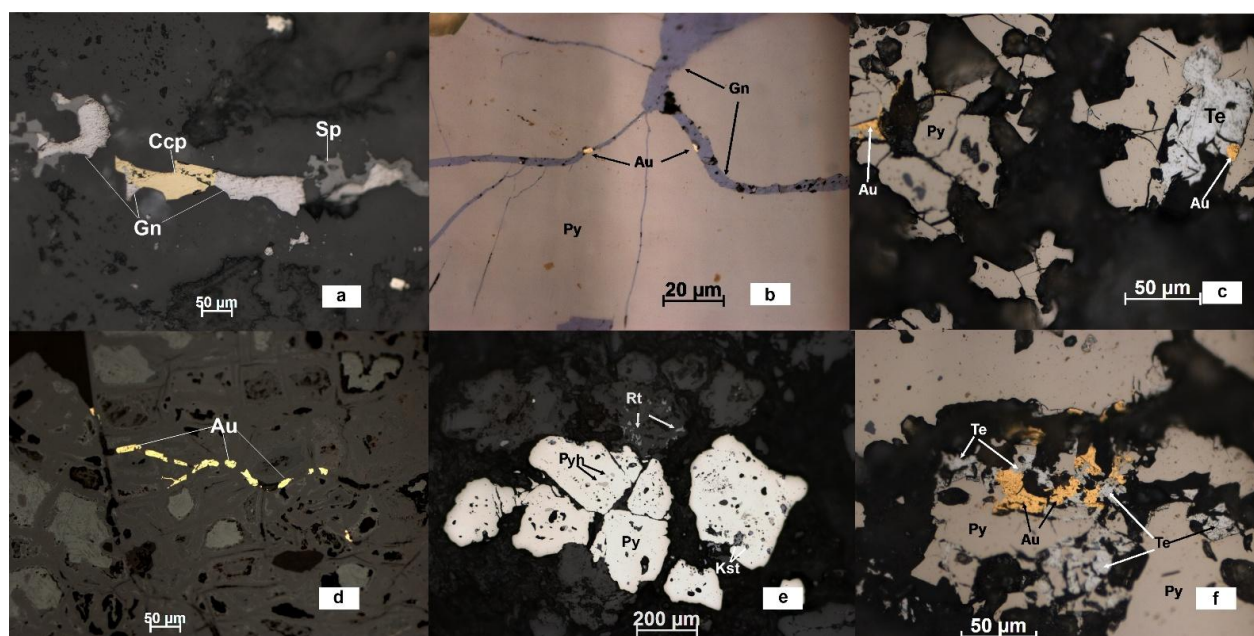


Figure 6. Microscopic images of mineral assemblages of gold, sulfides, and tellurides: (a) intergrowths of sphalerite, chalcopyrite, and galena veinlets in quartz; (b) galena veinlets containing gold inclusions and filling fractures in pyrite; (c) aggregates of corroded pyrite crystals with cavities filled with gold and tellurides enclosed in sericite; (d) gold veinlet in iron hydroxides; (e) cassiterite (Kst) and pyrrhotite (Pyh) in pyrite grains, with rutile (Rt) relics; (f) gold (Au) intergrown with telluride (Te) and pyrite (Py) in sericite

Molybdenite is a rare mineral and usually occurs as platy and flaky grains around quartz grains, as well as in intergrowths with pyrite II in quartz.

Covellite occurs as isolated fine-grained inclusions in the gangue matrix and among the oxidation products of chalcopyrite, as well as in rare individual grains and intergrowths with fine-grained cubic pyrite in the sericite matrix, reaching sizes of up to 0.07×0.1 mm. Covellite rims are observed around galena and sphalerite.

According to our observations, the vast majority of the principal carrier minerals of “invisible” gold belong to the early paragenetic assemblages. At the Kokkiya deposit, they are represented by a relatively uniformly distributed mass of fine-grained gold-bearing pyrite. Later generations of pyrite, including their disseminations within earlier fine-grained aggregates, are poorer in gold than the early pyrite, although they occasionally contain relatively coarse gold particles.

In the early pyrite assemblage, gold occurs predominantly in native form, whereas in later assemblages it is also associated with gold and silver tellurides (Fig. 6c).

Hypogene gold occurs:

a) as micron-scale inclusions in pentagonal dodecahedral pyrite grains;

b) as free gold in sericite and quartz, forming irregular and lumpy grains 0.005-0.1 mm in size;

c) as a component of gold and silver tellurides [46].

Native gold is pinkish-yellow in colour and is characterized by high fineness.

Supergene gold, in contrast, is localized in iron hydroxides and jarosite, forming so-called “spongy” gold with a yellowish-reddish colour (Fig. 6d). It occurs in association with jarosite and iron hydroxides. Most of this gold was deposited after these minerals, and to a lesser extent simultaneously with them.

In the oxidation zone of the ore bodies, gold occurs in iron hydroxide pseudomorphs after pyrite and develops along

oxidized zones. Spongy gold also occurs in pores and cavities of gangue mineral grains and as powdery masses in iron hydroxides. The composition of gold coated with iron hydroxides is, wt.%: Fe – 1.18; Cu – 0.06; Ag – 0.03; Au – 98.73; total – 100.00. In addition, so-called “mustard gold” was identified in aggregates with quartz, jarosite, mica, and, less commonly, pyrite. The composition of gold in a “coating” within quartz is, wt.%: Fe – 0.12; Cu – 0.13; Ag – 1.83; Au – 97.92; total – 100.00. Another variety of gold has the following composition, wt.%: Fe – 0.07; Cu – 0.17; Ag – 11.75; Au – 88.01; total – 100.00.

Tellurides and bismuth minerals are closely associated with pyrite. They occur as intergrowths with pyrite or as inclusions within its grains and may serve as positive indicators of gold mineralization.

Native gold is predominantly finely dispersed, up to 10 µm in size, and occurs enclosed in pyrite as well as in sericite and quartz (Fig. 6f). The formation of high-fineness gold veins and lenses is associated with supergene enrichment of primary gold in the oxidation zones.

At the late stage of mineral formation, fine inclusions of rutile, cassiterite, and pyrrhotite were identified in intensely corroded pyrite, in places reduced to isolated relics (Fig. 6e).

Gold commonly occurs in close association with various Te- and Bi-bearing minerals, predominantly calaverite (AuTe_2) and petzite (Ag_3AuTe_2). It occurs in several forms, including fine inclusions, veinlets, irregular grains up to 0.07 mm in size, and spongy aggregates up to 0.1 mm.

At depths of 140-143 m, gold, silver, and lead tellurides occur in sericitolites. These minerals are closely associated with native gold and develop in the intergranular spaces of intensely corroded pyrite III. In addition, rare high-temperature minerals, including molybdenite and arsenopyrite, were identified in close association with pyrite III.

The chemical composition of the main minerals studied is presented in Table 2.

Table 2. Chemical composition of the main minerals studied, wt. %

Main minerals studied	S	Fe	Ni	Cu	O	Al	Ca	Ag	Te	Au	Cd	Bi	Pb	Zn	Σ
Pyrite ($\text{Fe}_{0.82}\text{S}_{1.98}$)	51.95	45.83	—	0.45	—	—	—	—	—	—	—	—	—	0.37	98.6
Sphalerite ($\text{Zn}_{0.95}\text{S}_{1.02}$)	32.80	4.22	—	0.12	—	—	—	—	—	—	0.73	—	—	61.23	99.11
Galena ($\text{Pb}_{0.98}\text{S}_{0.98}$)	12.86	—	—	—	—	—	—	0.75	—	—	—	2.19	83.08	—	98.88
Gold (Au)	—	4.33	0.08	—	—	—	—	4.18	2.04	89.38	—	—	—	—	100
Petzite ($\text{Ag}_{2.85}\text{Au}_{1.09}\text{Te}_{1.94}$)	—	—	—	—	—	—	—	39.5	31.74	27.46	—	—	—	1.06	99.77
Altaite ($\text{Pb}_{0.83}\text{Te}_{0.78}$)	1.27	2.05	—	—	—	—	—	—	35.78	—	—	—	60.89	—	99.9
Calaverite ($\text{Au}_{0.9}\text{Te}_{1.9}$)	0.87	2.13	—	0.23	—	—	—	0.13	56.3	39.8	—	—	—	—	99.46
Bismuth oxide ($\text{BiO}_{4.2}\text{Fe}_{0.3}$)	—	4.24	—	—	21.62	0.31	0.40	—	—	—	—	73.44	—	—	100

4.3. Mineralogy of gold-telluride-sulfide ores

Tellurides at the Kokkiya deposit occur as fine grains and are commonly associated with native gold and sulfides. The most typical telluride minerals identified at the deposit are described below. Tellurium minerals are rare; their grain sizes are predominantly very small, and they commonly occur as inclusions in pyrite. Tellurium occurs in native form and as tellurides of gold (calaverite), bismuth (tsumoite), silver and gold (petzite), and lead (altaite); it was also identified in fahlores represented by goldfieldite. Elevated tellurium contents are characteristic of gold mineralization of epithermal and orogenic origin. The composition of tellurides may vary considerably.

Petzite (Ag_3AuTe_2) occurs in veinlets and pores of tennantite and also forms fine disseminations up to 1 μm in size within goldfieldite.

Tsumoite (BiTe) commonly contains selenium as an impurity.

Native tellurium occurs as inclusions of subhedral crystals 10–20 μm in size within pyrite and locally forms intergrowths with gold and silver tellurides. No isomorphic impurities were identified.

Tellurobismuthite (Bi_2Te_3) was documented in samples from deeper levels, at depths greater than 195 m.

Bismuthinite occurs as inclusions up to 10 μm in size within pyrite and may form intergrowths with the gold telluride calaverite.

Microanalysis of samples from depths of 9–10 m revealed a Bi-bearing mineral in iron hydroxides. It occurs as individual micron-scale inclusions and clusters 1–5 μm in size, with elongated or needle-like morphology, within pyrite and iron hydroxides, as well as larger grains measuring 10–20 $\times$ 40 μm and up to 10 $\times$ 50 μm . Bismuth also commonly forms fine disseminations in pyrite that are barely visible even at the maximum magnification of an optical microscope. Micron-scale gold is usually detected in such areas (Fig. 7).

Calaverite (AuTe_2) occurs between pyrite grains and has veinlet-like, oval, or prismatic morphology. It occurs both as isolated grains within the metasomatite and as intergrowths with gold and pyrite and may penetrate into pyrite, accompanied by its corrosion. Grain sizes reach 0.04 $\times$ 0.07 and 0.03 $\times$ 0.1 mm.

Altaite (PbTe) is the most widespread telluride at the Kokkiya deposit. It occurs as fine inclusions in corroded pyrite. The grains are irregular, locally veinlet-like in shape, and range from 5 to 60 μm in size. According to EDS analysis, the mineral consists predominantly of lead and tellurium, whose combined content is approximately 90 wt.%, confirming its identification as altaite (Fig. 8).

Gold and tellurides are spatially and genetically associated. In Figure 9, the telluride (point 003) is in direct contact with native gold (point 002), indicating their paragenetic relationship.

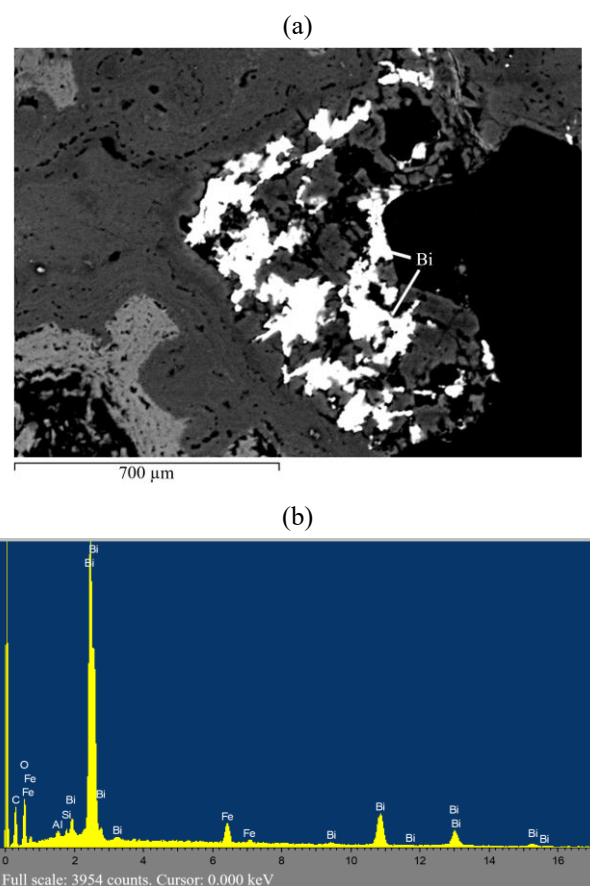


Figure 7. Bi-bearing phase in iron hydroxides: (a) micrograph of Bi-bearing phase occurrences; (b) EDS spectrum of the analysed phase

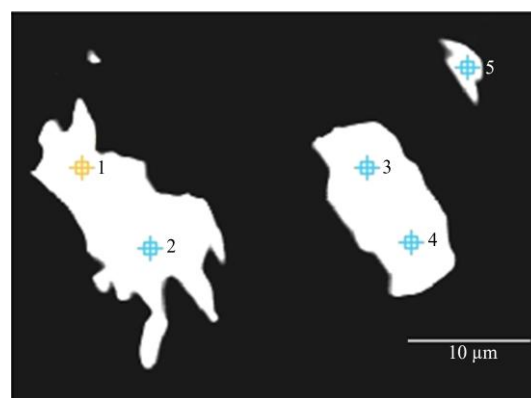


Figure 8. SEM micrograph of altaite (Alt) in a pyrite grain (Py), obtained with energy-dispersive spectroscopy (EDS)

The boundary between the minerals is irregular and corroded, which may indicate redistribution of components during late-stage hydrothermal reworking.

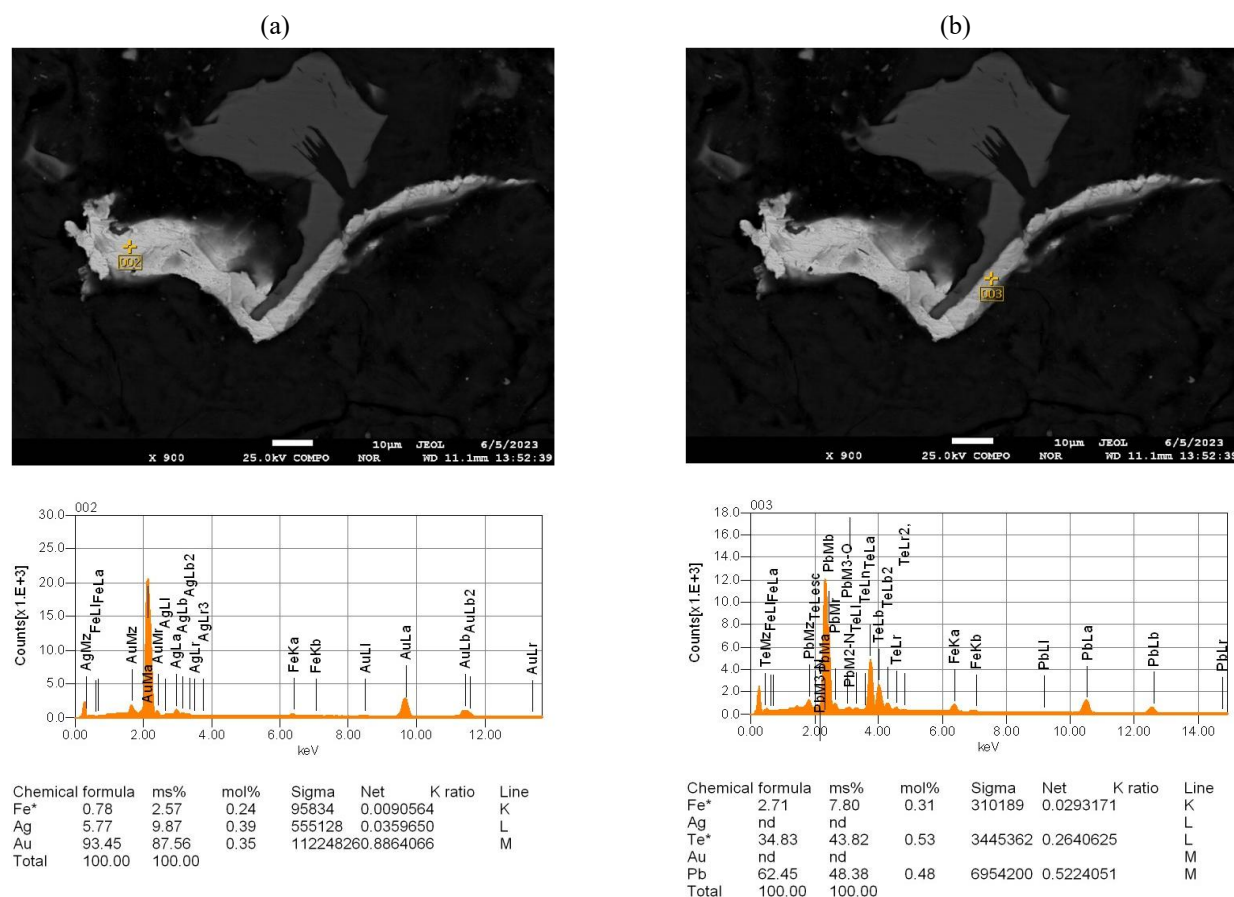


Figure 9. Micrograph of the distribution of tellurium (Te) and gold (Au), obtained by scanning electron microscopy with energy-dispersive spectroscopy (EDS)

Analytical data show that gold in this zone occurs in native form, with Au content of 93.45% and Ag content of 5.77%. Point 003 represents the lead telluride altaite (PbTe) with the following composition: Pb – 62.45%, Te – 34.83%. The high tellurium content confirms the presence of an independent telluride phase.

Gold and tellurides are spatially and probably genetically related. Native gold occurs adjacent to tellurides or in direct contact with them, which is a characteristic feature of telluride ore assemblages. The established relationship confirms the telluride type of gold mineralization, in which gold may occur both in native form and as a constituent of telluride minerals.

5. Discussion

The formation of the Kokkiya deposit is characterized by complex mineral parageneses and a multistage ore-forming process. The obtained results show that a significant proportion of high-fineness native gold is associated with the early mineral assemblages of the main ore stage. Gold precipitation probably occurred as a result of destabilization of gold-bearing hydrosulfide complexes during cooling and changes in the physicochemical parameters of the mineral-forming fluid. The decrease in the overall amount of gold in later assemblages may have resulted from fluid neutralization during interaction with the host rocks.

The presence of numerous paragenetic associations and morphogenetic types of native gold in combination with tellurides indicates a multistage process of gold mineralization and suggests the possible continuation of productive mineralization at deeper levels. The mineral-forming sequence estab-

lished for the Kokkiya deposit is generally comparable with that described for the Bereznjakovskoe Au-Bi-Te ore field [4] and for the Kochbulak and Kairagach deposits [5]–[7].

Gold commonly occurs in native form; however, in gold-telluride deposits, a significant proportion of gold is spatially and paragenetically associated with telluride minerals. The formation of such phases is controlled by temperature, pressure, redox conditions, and the composition of the hydrothermal fluid [47]–[50]. Studies of gold-telluride systems suggest that their evolution can be conditionally divided into several successive stages:

- an early quartz-pyrite stage characterized by the formation of quartz veins and disseminated pyrite, with only limited development of telluride mineralization;
- an intermediate quartz-sulfide stage during which cooling, reduction, and possible fluid mixing are accompanied by the precipitation of gold and sulfides and by changes in the physicochemical conditions;
- a late gold-telluride stage associated with decreasing temperature and pressure and changes in redox conditions, which promote destabilization of gold-telluride complexes and crystallization of telluride minerals.

The obtained results suggest that the gold-bearing hydrothermal fluid transported gold and tellurium in dissolved form. As the fluid ascended and cooled, and as it interacted and possibly mixed with other fluids, the physicochemical conditions changed, including pH and Eh. Under these conditions, gold-telluride complexes became unstable, promoting the precipitation of telluride minerals.

Tellurides formed predominantly during the later stages of mineral formation under decreasing temperature and changing redox conditions, commonly together with native gold. This sequence is in good agreement with the established structural and paragenetic relationships among the minerals of the Kokkiya deposit.

Pyrite is the principal ore mineral of the deposit and is represented by several generations that differ in morphology, textural features, and mineral associations. In gold-telluride deposits, gold tellurides commonly form paragenetic associations with different generations of pyrite. According to published data, gold-telluride mineralization generally forms under medium- and low-temperature hydrothermal conditions, whereas Au- and Ag-rich telluride-sulfosalt assemblages are characteristic of relatively late stages of ore formation [48], [49].

At the Kokkiya deposit, a significant proportion of native gold apparently precipitated during the pyrite stage at the beginning of ore mineralization. Simultaneous precipitation of pyrite and other sulfides may have reduced sulfur activity in the residual fluid and resulted in its relative enrichment in tellurium. The main tellurides associated with gold formed during a gradual decrease in temperature and sulfur fugacity and an increase in tellurium activity.

Altaite probably formed somewhat earlier than the other telluride minerals under relatively low tellurium activity. Further changes in the physicochemical conditions of the fluid allowed the formation of other Te- and Bi-bearing phases, including tsumoite and tellurobismuthite. Calaverite (AuTe_2), one of the characteristic gold tellurides, is associated mainly with the late stages of the hydrothermal-metasomatic process. At the Kokkiya deposit, gold tellurides are most characteristic of the telluride-polymetallic and late pyrite-polymetallic stages, whereas a significant proportion of native gold is associated with the early ore stage, as confirmed by the established paragenetic relationships among the minerals (Table 1).

Supergene mineralization is represented by jarosite, goethite, and hydrogoethite. Within the supergene zone, gold tends to undergo compositional changes and an increase in fineness due to partial removal of silver and other impurities [51]. Such gold generally does not form massive accumulations; instead, spongy, moss-like, and powdery forms are characteristic. One of the reliable criteria for distinguishing hypogene from supergene gold is the nature of mineral parageneses and structural relationships among the minerals. Supergene gold is characterized by intergrowths with iron hydroxides and by the development of thin films and precipitates in mineral pores and fractures.

Changes in gold fineness during supergene alteration of ores have been repeatedly reported in the literature. In particular, supergene "refining" of gold has been described, resulting mainly from the preferential removal of silver from primary gold grains [52], [53]. Albov [53] reported an increase in gold fineness within the oxidation zones of sulfide-quartz deposits in the Urals. According to his data, oxidized ores of the Kochkar deposit contain gold with a fineness of approximately 870-900‰, whereas gold in the primary ores has a fineness of approximately 700‰. Similar changes in gold fineness have also been reported from other gold deposits.

For the Kokkiya deposit, a relationship between gold fineness, depth, and mineral association has also been established. Gold enclosed in late galena veinlets between grains

of aggregate pyrite IV at depths of 110-140 m is of moderately high fineness, with an average value of approximately 810‰. At shallow depths (6-8 m), finely dispersed gold enclosed in pentagonal dodecahedral pyrite III within sericitolites has lower fineness [54]. The obtained results are consistent with the concept that gold fineness and composition may vary depending on the physicochemical conditions of mineral formation, subsequent remobilization, and paragenetic mineral associations [25], [55]-[58].

Hydrothermal systems evolve both temporally and spatially as a result of changes in temperature, pressure, and redox conditions. Three-dimensional modelling of gold solubility and fineness shows that vertical variations in gold composition within ore zones may reflect the physicochemical evolution of hydrothermal fluids [55]. Rapid cooling and fluid mixing can cause marked changes in the conditions of gold precipitation even over relatively small depth intervals.

Late hydrothermal and metamorphic processes may additionally modify the primary Au-Ag relationships. Remobilization of noble metals, including redistribution of silver relative to gold, can alter the original gold fineness [56]. As a result, zones of increased fineness may form not only during primary precipitation but also through post-ore remobilization and recrystallization.

Thus, vertical variations in gold fineness should be regarded as the result of the combined effects of primary mineral-forming conditions and subsequent hydrothermal and supergene alteration. Comparison of gold fineness with mineral assemblages and stages of mineral formation can be used to reconstruct the evolution of the ore-forming system and assess the prospectivity of deeper levels of the deposit [25], [57]-[59].

6. Conclusions

Mineralization at the Kokkiya deposit developed during two main stages, hypogene and supergene. Within the hypogene stage, four successive stages of mineral formation were distinguished: the pre-ore stage, represented mainly by quartz-sericite metasomatites; the early pyrite stage, characterized by widespread pyrite and native gold; the main telluride-polymetallic stage, associated with the formation of gold, silver, lead, and bismuth tellurides together with native gold and corroded pyrite; and the late pyrite-polymetallic stage, characterized by the development of galena, sphalerite, chalcopyrite, and associated gold-silver mineralization.

Pyrite is the principal ore mineral of the deposit and is represented by several generations that differ in morphology, textural characteristics, and mineral associations. A significant proportion of native gold is associated with early pyrite mineralization, whereas the tellurides calaverite, petzite, altaite, and tsumoite are most characteristic of the later stages of ore formation. They are closely associated with native gold and are mainly confined to corroded pyrite grains, filling intergranular spaces, pores, and fractures. The presence of Te- and Bi-bearing minerals can therefore be considered an important indicator of gold mineralization.

A relationship was established between gold mineralization and the nature of metasomatic alteration of the host rocks. The richest mineralized zones are confined to the inner and most intensely altered parts of the metasomatic zonation. Sericitolites, characterized by elevated gold contents, may be used as a mineralogical exploration criterion when evaluating prospective areas of the deposit.

Native gold shows different modes of occurrence and compositions depending on the stage of mineral formation and mineral association. In oxidized ores at depths of 9-10 and 20-22 m, the fineness of gold enclosed in iron hydroxides ranges from 634 to 820‰. Gold intergrown with altaite and calaverite between pyrite grains has a higher fineness of 944-977‰, whereas values of approximately 810‰ were determined in late galena-pyrite veinlets. These differences indicate that gold fineness is controlled not only by depth but also by the stage of mineral formation, mineral association, and subsequent supergene alteration.

Supergene gold is mainly associated with iron hydroxides and jarosite and occurs as spongy, porous, and powdery particles. The identified features of its morphology and composition, together with the nature of its mineral parageneses, make it possible to distinguish supergene gold from hypogene gold and to assess the degree of alteration of primary mineralization within the oxidation zone.

EDS mapping and electron-probe studies made it possible to refine the localization of micron-scale gold and telluride inclusions and to establish their spatial relationships with pyrite and other sulfides. The combined use of data on the stages of mineral formation, pyrite generations, gold composition and fineness, and the distribution of telluride mineralization refines the mineralogical-genetic model of the Kokkiya deposit and can be used to assess the potential continuation of productive gold-telluride mineralization at depth.

Author contributions

Conceptualization: GO; Data curation: SA; Formal analysis: AS; Funding acquisition: ST, YA; Investigation: GO, SA; Methodology: BS; Project administration: GO; Resources: GO, SA, ST, YA; Software: GO, AS, YA; Supervision: GO, SA; Validation: GO, BS; Visualization: AS; Writing – original draft: GO, BS, SA, YA; Writing – review & editing: GO, AS, ST. All authors have read and agreed to the published version of the manuscript.

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Conflicts of interest

The authors declare no conflict of interest.

Data availability statement

The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

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Мінералогія золото-телуридно-сульфідних руд родовища Коккія, Казахстан

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Мета. Встановити послідовність мінералоутворення та уточнити особливості формування золото-телуридно-сульфідної мінералізації родовища Коккія на основі вивчення мінеральних асоціацій, типоморфних ознак рудних мінералів, форм знаходження самородного золота й телуридів, а також їх просторових і парагенетичних взаємовідношень.

Методика. Досліджено 120 зразків руд і вміщувальних порід із ядра бурових свердловин. Застосовано оптичну мікроскопію у відбитому та прохідному світлі, сканувальну електронну мікроскопію, електронно-зондовий мікроаналіз, EDS/WDS-аналіз та EDS-картування. Додатково зіставлено пробність і склад золота з глибиною залягання, генераціями піриту, структурно-текстурними особливостями руд, а також гіпогенними й гіпергенними мінеральними асоціаціями.

Результати. Виділено два основні етапи мінералізації – гіпогенний і гіпергенний. У межах гіпогенного етапу встановлено чотири послідовні стадії: дорудну гідротермально-метасоматичну, ранню піритову, основну телуридно-поліметалічну та пізню пірит-поліметалічну. Головним рудним мінералом є пірит, представлений кількома генераціями, що відрізняються морфологією та парагенезисом. Самородне золото пов'язане з піритом, кварцом, серицитом, галенітом і телуридами. Для пізніх стадій характерні калаверит, петцит, алтаїт, цумойт, самородний телур і Ві-вмісні мінерали. Пробність золота у зростках з алтаїтом і калаверитом становить 944-977%, тоді як в окиснених рудах – 634-820%. EDS-картування підтвердило тісний просторовий зв'язок мікронних включень золота й телуридних фаз. Найінтенсивніша мінералізація приурочена до внутрішніх, найбільш змінених частин метасоматичної зональності.

Наукова новизна. Уточнено мінералогічно-генетичну модель родовища Коккія шляхом узгодження генерацій піриту, пробності золота, телуридної мінералізації та послідовності рудоутворювальних стадій. Показано, що розподіл золота й телуридів відображає багатостадійну еволюцію гідротермальної системи та подальші гіпергенні перетворення.

Практична значимість. Серицитоліти, Те- і Ві-вмісні мінерали, особливості генерацій піриту та золото-телуридні асоціації можуть використовуватися як мінералогічні пошукові критерії під час оцінювання перспективних зон і можливості збереження продуктивної мінералізації на глибині.

Ключові слова: генезис родовища; мінералізація; самородне золото; телуриди; сульфіди; метасоматити

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