Mineralogy, Geochemistry and Localization of Regional Pyritization Zones – Constraints from Early Mesozoic Deposition in the Chay–Yureya Fault of the Kular-Nera Terrane, NE Russia

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Abstract. The Early Mesozoic clastic rocks the Kular-Nera terrane in the Verkhoyansk-Kolyma orogenic belt, northeast Russia, exhibit regional sulfidation zones. The most abundant mineral of the zones is pyrite. However, its origin (sedimentary-diagenetic, metamorphogenic-hydrothermal, metasomatic) and contribution to the formation of economically important gold deposits remain debatable. The localization of the sulfidation zones is still poorly understood. We have studied geological-structural and mineralogical-geochemical features of pyritization zones in bedrock outcrops on Khara-Yuryakh creek (a right-side tributary of the Nera river) within the Kular-Nera terrane, Verkhoyansk-Kolyma folded area. The pyritization zones are distant from the known gold deposits, and they extend along the Chay-Yureya regional fault. The deformation structure of the clastic rocks of the Chay-Yureya fault is defined by different-aged fold-thrust and strike-slip elements. The early deformations are isoclinal and tight folds up to a few hundred meters wide, with rounded and sharp crests and subhorizontal hinges. The early folds were refolded so that their crests may be seen on the limbs of later folds of the same NW strike. These structures were formed in the conditions of progressive deformation D1 in course of a single continuous (non-stop) tectonic regime during the frontal convergence of the Kolyma-Omolon superterrane with the eastern margin of the Siberian craton. These are commonly inclined or, more rarely, recumbent folds. Also present are late folds associated with dextral and sinistral strike-slip motions on the Chay-Yureya fault. The sulfide mineralization of the Chay-Yureya fault is represented by the disseminated idiomorphic pyrite crystals 1 to 10 mm in size. Metapyrites exhibit a cataclastic microtexture complicated by later corrosion processes. They contain zircon, rutile, and monazite microinclusions entrained in the process of growth. Microinclusions of galena, sphalerite, chalcopyrite, and other late sulfides are confined to defects in the pyrite grains. The chemical composition of pyrite was determined on the Camebax-Micro microanalyzer, using a standard X-ray spectral analysis (DPMGI, SB RAS, Yakutsk). Most of the grains have a stoichiometric composition. 30 percent of the analyses showed excess Fe. Metacrystals of pyrite demonstrate variations in the concentration of trace elements, which often leads to chemical zonality. Our investigations showed that pyritization zones of the rocks are localized in the trans-crustal Chay-Yureya fault which served as a transit path for ascending regional fluid flows. Typomorphic trace elements found in pyrites are Co, Ni, As, Sb, and Cu, with the total amount of 0.1 to 0.4%. They are characterized by the low concentrations and non-uniform distribution. Zonality in the distribution of trace elements is attributable to the poly-
stage growth of pyrite metacrystals. The diagenetic stage was accompanied by accumulation of Co, As, and Sb in the central zones of crystals, while during the metamorphogenic-hydrothermal stage, Ni and As were accumulated in the outer zones.

1. Introduction

Disseminated mineralization in the Kular-Nera terrane, Verkhoyansk-Kolyma folded area, northeast Russia, was studied within the limits of well-known orogenic gold deposits such as Malo-Tarynskoe [1, 2], Drazhnoe [3], Sana [4], Levoberezhnaya Zone [5] and Vyyn [6]. The mineralization is localized within the fault zone and hosted by Early Mesozoic clastic rocks. The host alteration is sericite-chlorite-quartz in composition. The main ore minerals are auriferous pyrite and arsenopyrite. Gold is mostly invisible. Disseminated mineralization of uncertain origin is also found in sites far apart from the known gold ore districts [7-10]. This fact permits expansion of the area of prospecting work but requires the elaboration of clear criteria for an estimation of the gold content of these potential sites of mineralization. The most abundant mineral in the sulfidation zones of the rocks is pyrite. However, its origin (sedimentary-diagenetic, metamorphogenic-hydrothermal, metasomatic) and contribution to the formation of economically important gold deposits remain debatable. The localization of the sulfidation zones is still poorly understood. We have studied geological-structural and mineralogical-geochemical features of pyritization zones in bedrock outcrops on Khara-Yuryakh creek (right-side tributary of the Nera river) within the Kular-Nera terrane, Verkhoyansk-Kolyma orogenic belt (Figure 1).

![Figure 1](image-url)

Figure 1. (A) Location of the study area; (B) Geological sketch map of the area of the lower Khara-Yuryakh creek (compiled based on the data of Protopopov, R. I.)
2. Methods

Structural-kinematic studies were conducted using up-to-date methods [11-14]. Measurements of planar and linear structures (bedding, cleavage, faults, fold hinges, etc.) were made. The structural data were statistically analyzed and plotted on the upper hemisphere of the Wulff stereographic net.

Rock sampling was conducted in bedrock exposures in the lower reaches of Khara-Yuryakh creek (Figure 1). Preparation of samples for analyses was made at the Diamond and Precious Metal Geology Institute of the Siberian Branch of the Russian Academy of Sciences (DPMGI, SB, RAS, Yakutsk). Thick polished sections (10 in number) were prepared for mineralogical and geochemical studies. Textural-structural analysis of mineralization was made using a ZEUS Axio optical microscope. Chemical composition of minerals was determined on a JEOL JSM-6480LV scanning electron microscope equipped with an Energy 350 Oxford energy dispersion spectrometer (20 kV, 1 nA, diameter 1 µm) (DPMGI, SB, RAS, Yakutsk) and on a Camebax-Micro microanalyzer using an X-ray spectral analysis (DPMGI, SB, RAS, Yakutsk). Au and Ag contents were determined in powdery monomineralic samples by the method of atomic-absorption spectrometry with electrothermal atomization using a ThermoScientific iCE 3500 spectrometer (DPMGI, SB, RAS, Yakutsk). Detection limits of elements are 0.0001 g/ml and higher.

3. Results and discussion

3.1. Deformation structures

In the lower course of Khara-Yuryakh creek, we studied fold-fault deformations of the rocks in the regional sulfidation zone of the Chay-Yureya fault. The fault separates the Polousny-Debin and the Kular-Nera terranes located between the western margin of the Siberian craton and the Kolyma-Omolon superterrane. The Polousny-Debin terrane is composed of Jurassic flysch deposits (siltstone, mudstone, sandstone), and the Kular-Nera terrane is built of Late Jurassic clastic rocks (Figure 1). The Chay-Yureya fault has an NW and rarely sublatitudinal trend, and is conformable to the orientation of folds. It is expressed as a wide (up to 7-10 km) zone of intense folding and faulting, dynamometamorphism, pyritization, hydrothermal activity as well as swarms of dikes of acid, intermediate, and basic composition. There are rare granitoid plutons confined to the fault. The Chay-Yureya fault controls localization of gold ore occurrences and large placer gold deposits. It is a long-lived fault. It is established that it affected sedimentation conditions and the development of syn-sedimentary deformation. Variously directed motions on the fault occurred in Late Jurassic-Cretaceous time [15].

In the zone of regional sulfidation of the Chay-Yureya fault rocks, we observed fold-thrust deformations in a low-grade metamorphic setting characteristic of the SE sector of the Kular-Nera terrane [16-19]. Vergence of the folds varies from SW (Figure 2 A) to NE (Figure 2 C), and the width attains a few meters. The presence of large folds up to a few hundred meters wide is supposed northwestward from Khara-Yuryakh creek [16]. The folds have subhorizontal hinges of NW orientation. No cleavage associated with the early folds is observed. The early folds and bedding-plane detachment faults are deformed into folds with gently inclined and subhorizontal axial surfaces (Figure 2 E, F). These are normally NW-striking lying and overturned chevron folds with low-angle hinges. The folds associate with extensive thrusts of SW and NE vergence [16]. An NW-striking non-pervasive fracture cleavage related to the folds is observed (Figure 2 A, B, D). It is most intensive in mudstones less developed in siltstones, and absent in sandstones.
Figure 2. Deformations of Upper Triassic rocks in the lower course of Khara-Yuryakh creek

(A, C) inclined folds F1/1; (B, D) non-pervasive fracture cleavage S1/2; (E, F) recumbent chevron folds F1/2. Planar structures (S) are given as dip azimuth/dip angle (e.g., 55/31 denotes eastward dip at 31°). For linear deformation elements (b), denotation plunge azimuth/plunge angle is used (e.g., 160/3 means plunge azimuth of 160° and plunge angle of 3°). Signs S1/1 (S1/2) and b1/1 (b1/2) denote the relation of a structural element to a particular deformation event of stage D1.
The described fold-thrust structures are cut by gabbroid dikes similar to the Late Jurassic (150±3 Ma, U-Pb zircon, [20]) dikes of the Vyun ore field. Considering these and the above given structural data we assume that the described fold-thrust deformation events occurred no later than the end of the Late Jurassic (Tithonian) in the conditions of a single continuous (non-stop) tectonic regime during frontal convergence of the Kolyma-Omolon superterrane with the eastern margin of the Siberian craton. All mentioned above and close orientation of the folds suggest that the early fold-thrust structures (F1/1, S1/1, F1/2, S1/2) were formed under conditions of progressive deformation D1 (Figure 3). Such a possibility of the formation of complex folds during progressive deformation is described in [21, 22].

In the SE sector of the Kular-Nera terrane, one can observe deformations associated with sinistral and dextral motions on the Chay-Yureya fault [16, 17, 19]. They are superposed on the early Late Jurassic deformations. In outcrops in the Khara-Yuryakh creek area, there are noted bedding-plane detachment faults and horizontal slickenlines on the limbs of early folds.

3.2. Mineralogy and geochemistry of disseminated mineralization
The sulfide mineralization of the Chay-Yureya fault is represented by abundant disseminated idiomorphic cubic pyrite crystals 1 to 10 mm in size. A cataclastic microtexture is well developed, and is complicated by later corrosive processes. Pyrite metacrystals contain microinclusions of zircon, rutile, and monazite entrained during the crystal growth. Galena, sphalerite, chalcopyrite and other late sulfides are confined to defects in crystals.

The X-ray spectral analysis of pyrites revealed their typomorphic trace elements: Co, Ni, As, Sb and Cu, with the total amount of 0.1 to 0.4% (Table 1). In most of the grains, the pyrite formula is close to stoichiometric [(Fe0.99Co0.002)0.992(S2.00As0.003)2.003]. 30 percent of the analyses showed excess Fe. A constant impurity in the pyrite composition is Co ranging in content from 0.02 to 0.1%, with a considerable degree of dispersity (ν=30%). The Ni impurity (Cmin=0.002%; Cmax=0.19%) is established in 76% of the grains. The As impurity is rare, some of the crystals belong to As-free varieties. In 60% of the analyses, the As content varies from 0.05 to 0.15%. Cu concentrations in the studied crystals are 0.01 to 0.03%. The Sb content varies from 0.001 to 0.05%. In 65% of the analyses C_{Sb}=0.01-0.03%.
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Elevated Sb contents are noted in pyrites with excess Fe. The atomic-absorption analysis revealed the presence of gold \( (Au_{max}=0.37 \text{ ppm}) \) and silver \( (Ag_{max}=1.5 \text{ ppm}) \) in pyrite metacrystals.

| Kh-Yu-14 | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Ng | Fe | S | Co | Ni | Cu | Sb | As | Fe | S | Co | Ni | Cu | Sb | As |
| 1 | 46.69 | 53.53 | 0.048 | 0.01 | bdl | bdl | 0.047 | 1.1 | 46.19 | 53.62 | 0.067 | 0.023 | 0.001 | 0.030 | bdl |
| 2 | 46.77 | 53.97 | 0.104 | 0.022 | 0.008 | 0.019 | bdl | 2 | 46.51 | 53.86 | 0.063 | 0.002 | bdl | 0.017 | bdl |
| 3 | 46.59 | 53.91 | 0.096 | 0.022 | 0.022 | 0.02 | bdl | 3 | 46.65 | 53.67 | 0.065 | bdl | bdl | 0.019 | bdl |
| 4 | 46.85 | 53.62 | 0.047 | bdl | 0.029 | 0.018 | bdl | 4 | 46.24 | 53.02 | 0.053 | 0.007 | bdl | 0.050 | bdl |
| 5 | 47.1 | 53.78 | 0.049 | 0.01 | 0.003 | 0.013 | bdl | 5 | 46.42 | 53.16 | 0.062 | 0.021 | bdl | 0.041 | bdl |
| 6 | 46.75 | 53.58 | 0.065 | 0.04 | bdl | 0.021 | 0.075 | 6 | 46.23 | 52.50 | 0.082 | 0.003 | 0.011 | 0.030 | bdl |

Variations in the concentration of trace elements in pyrite metacrystals produced chemical zonality (Figure 4). The central zone of the crystals is characterized by maximum Co values, which is due to isomorphic incorporation of Co into pyrite composition in reducing conditions at the stage of diagenesis. The middle zone is rich in antimony and arsenic. High contents of these elements are characteristic of the Upper Triassic rocks of the study area. The outer zone is enriched in arsenic \( (C_{As}=0.29 \% ) \) and nickel \( (C_{Ni}=0.18) \) which is likely due to their input by metamorphic-hydrothermal fluids. No strict zonation is observed in Cu distribution. There are sites rich in Cu and those with a minimum Cu content. This fact reflects a high migration capacity of copper.

Scanning of crystals was made along with profiles. Numbers of analytical points correspond to those in Table 1. No strong correlation was observed between concentrations of trace elements within a single pyrite crystal. However, analysis of all data obtained on the trace element distribution revealed local trends of the close correlation between concentrations of element pairs (Figure 5). The trends correspond to the zones of crystal growth. In the middle part of the grains, a positive correlation is evident between As and Sb concentrations \( (r=0.81) \) (Figure 5, A). In the outer zone, a direct correlation is seen distinctly between Ni and As \( (r=0.84) \) (Figure 5, G) and negative correlation is observed between Co and Ni \( (r = -0.98) \) (Figure 5, H). Significant variations in the content of trace elements in pyrite and regularities in their distribution result from changing physico-chemical conditions of mineral formation and suggest a poly-phase growth of pyrite metacrystals.
|       | Kh-Yu-14 | Kh-Yu-18 | Kh-Yu-19 |
|-------|----------|----------|----------|
| Co    | ![Co](image) | ![Co](image) | ![Co](image) |
| Ni    | ![Ni](image) | ![Ni](image) | ![Ni](image) |
| As    | ![As](image) | ![As](image) | ![As](image) |
| Cu    | ![Cu](image) | ![Cu](image) | ![Cu](image) |
| Sb    | ![Sb](image) | ![Sb](image) | ![Sb](image) |

**Figure 4.** Pyrite metacrystals and their trace-element distribution

Scanning of crystals was carried out by profiles. The data was processed in the Surfer program. Interpolation method – Triangulation with Linear Interpolation.
Figure 5. Scatterplots of: (A) As vs. Sb; (B) Sb vs. Cu; (C) Sb vs. Ni; (D) Sb vs. Co; (E) As vs. Cu; (F) Cu vs. Ni; (G) As vs. Ni; (H) Ni vs. Co; (I) As vs. Co. Lines show correlation trends

4. Conclusions
The data obtained indicate a spatial association of the regional zones of disseminated sulfidation with major faults. Our investigations showed that pyritization zones of the rocks are localized in the transtensional Chay-Yureya fault, which served as a transit path for ascending regional fluid flows. A number of deformation events are recognized. The early deformations are isoclinal and tight folds up to a few hundred meters wide, with rounded and sharp crests and subhorizontal hinges. The early folds were refolded so that their crests may be seen on the limbs of later folds of the same NW strike. These are commonly inclined or, more rarely, recumbent folds. The fold-thrust structures (F1/1, S1/1, F1/2, S1/2) were formed in the conditions of progressive deformation D1 in the course of a single continuous (non-stop) regime, during the frontal convergence of the Kolyma-Omolon superterrane with the eastern margin of the Siberian craton. Also present are late folds associated with dextral and sinistral strike-slip
motions on the Chay-Yureya fault. Typomorphic trace elements in pyrite metacrystals include Co, Ni, Sb, As, and Cu. They are characterized by low concentrations and non-uniform distribution. Zonality in the distribution of trace elements is attributable to the poly-stage growth of pyrite metacrystals. The diagenetic stage was accompanied by accumulation of Co, As, and Sb in the central zones of crystals, while during the metamorphogenic-hydrothermal stage Ni and As were accumulated in the outer zones. The development of local close-correlation trends characterizes a change in PT conditions throughout the formation period of the regional sulfidation zones.

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