Isotopic-geochemical characteristics of quartz and pyrite in the Upper Carboniferous rocks of South Verkhoyanye, Northeast Russia: an insight into the genesis of veinlet-disseminated mineralization

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Abstract. Discussed are characteristics of veinlet-disseminated mineralization in the northern part of South Verkhoyanye, in the sections located far away from the known gold deposits. The mineralization is represented mainly by quartz and pyrite enclosed in the Upper Carboniferous terrigenous rocks. Mineralogical-geochemical studies of mineralization are made, and isotopic compositions of oxygen in quartz and sulfur in pyrite are determined. The main trace elements in pyrite are Co, Ni, and Sb, with rare As, Cu, and Zn. Quartz contains significant amounts of Sr, W, and Co. The REE content in quartz is an order of magnitude higher than that seen in chondrites. Pyrite is light in sulfur isotopic composition (δ34S = -2.7...-7.1‰). Quartz contains isotopically heavy oxygen (δ18O = 18.2-19.1‰). The data obtained indicate that the veinlet-disseminated mineralization hosted by the Upper Carboniferous rocks in the northern South Verkhoyanye was developed as a result of metamorphogenic-plutonogenic processes.

1. Introduction
The Upper Carboniferous terrigenous rocks of South Verkhoyanye extend in a narrow band along the western boundary of the South Verkhoyansk tectonic zone, and are the host for orogenic gold deposits (OGD) [1, 2] (Figure 1). They were formed in a passive continental margin environment, replacing largely carbonate strata characteristic of the Early and Middle Paleozoic stages in the development of the eastern margin of the North Asian craton. Lithological heterogeneity, accumulation in the deltaic facies conditions, and enrichment in some ore-forming elements (As, Pb, Cr, Sb, Zn) are typical of the rocks. Structural-metamorphic reworking of the rocks is confined to the zones of intense fold-and-fault deformation (shear zone) [3, 4].

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The veinlet-disseminated mineralization is localized in the northern part of South Verkhoyanye, at a considerable distance from the known gold deposits, in sections made largely of siltstone with interbeds and lenses of calcareous sandstone belonging to the Ekachan Formation of Upper Carboniferous age. Mineralogical-geochemical analysis of mineralization was made and compositions of stable isotopes of oxygen ($\delta^{18}O$) in quartz and sulfur ($\delta^{34}S$) in pyrite were determined.

Figure 1. Geological sketch map of the central part of the South Verkhoyanye. The inset shows the position of the area of works. VFTB – Verkhoyansk fold-and-thrust belt; OT – Okhotsk terrane; KNSB - Kular–Nera slate belt; PDT– Polousno–Debin terrane

Electron microprobe analysis was performed using a Camebax microanalyzer (Cameca, Courbevoie, France) and a JEOL JSM-6480LV scanning microscope (JEOL, Tokyo, Japan). Trace elements and REE in quartz were analyzed by LA-ISP-MS ELAN-9000 (Perkin Elmer, USA). Both absolute values and chondrite-normalized abundance ratios were obtained.

2. Results and discussion
In northeast Russia, there are abundant sulfidization zones in the Upper Paleozoic and Lower Mesozoic carbonaceous terrigenous rocks of the Verkhoyansk Complex. Some of the large gold deposits in the area are found to be localized within the regional sulfidization zones often of unclear origin [5]. This characteristic feature can be interpreted as the main factor in the formation of orogenic gold deposits.
Figure 2. Photographs (A, B, C), photomicrographs (D, E, F), and backscattered electron images (G, H, I, J, K, L) of the mineral assemblage. A – quartz-carbonate veinlets; B – banded quartz vein; C – pyrite nodule in siltstone; D – fragment of zoned spheroidal pyrite; E – idiomorphic pyrite crystals and intergrowths and a quartz veinlet; F – frambooidal pyrite aggregates in siltstone; G-I – galena inclusions in pyrite aggregates; J – octahedral pyrite crystals in the center of a framboid; K-L – chalcopyrite and galena inclusions in cubic pyrite crystals.

The mineralization is hosted in the terrigenous rocks and includes mainly quartz and pyrite. Quartz forms sets of zoned and banded quartz, quartz-carbonate, and quartz-chlorite veinlets (Figure 2A, B). The host rocks are brecciated in the vein selvages. Pyrite in the siltstones occurs as zoned spheroidal concretions (Figure 2C, D), bedding-parallel veinlets, idiomorphic cubic crystals (Figure 2E), and rare frambooids (Figure 2F, G). Pyrite contains microinclusions of later sulfides such as chalcopyrite, sphalerite, and galena. Chalcopyrite is the most widespread mineral inclusion, particularly in cubic pyrite crystals. The sphalerite aggregates, which are often localized in fractures in pyrite, have grey internal reflections. Sphalerite contains Fe (1.5-4.5%). Galena is the latest of the observed minerals. It occurs as microinclusions in pyrite and chalcopyrite, and also replaces the central part of frambooidal pyrite (Figure 2 H, I, K, L).
Pyrite has almost a stoichiometric chemical composition (Table 2). S/Fe values in all pyrites display unimodal distribution. The main trace elements in pyrite are Co, Ni, and Sb, with rare As, Cu, and Zn. Co is found in all of the studied samples. Pyrite exhibits significant variations in Co and Ni abundances, which determine the value of the Co-Ni genetic index (Figure 3). 10% of the analyzed pyrite grains contain Co>0.1%. In most of the grains, the Co/Ni ratio varies within the range of 0.1-2.0, which is typical of pyrite of metamorphogenic-hydrothermal origin.

Table 1. Average chemical composition of pyrites, wt%

|       | Q-25, n=34 | Q-33, n=24 | Q-34, n=23 | Q-38, n=23 | Q-41, n=13 | Q-44, n=22 |
|-------|------------|------------|------------|------------|------------|------------|
| Fe    | 46.65      | 46.61      | 46.71      | 46.61      | 46.19      | 46.32      |
| S     | 52.64      | 53.42      | 53.87      | 53.85      | 53.41      | 53.40      |
| Co    | 0.11       | 0.06       | 0.06       | 0.06       | 0.06       | 0.04       |
| Sb    | 0.05       | 0.03       | 0.03       | 0.06       | 0.06       | 0.03       |
| As    | 0.07       | 0.13       | 0.07       | 0.07       | 0.07       | 0.11       |
| Ni    | 0.09       | 0.10       | 0.17       | 0.03       | 0.03       | 0.14       |
| Cu    | 0.02       | 0.01       | 0.01       | 0.01       | 0.01       | 0.02       |
| Zn    | 0.01       | 0.01       | 0.01       | 0.01       | 0.01       | 0.03       |
| Total | 99.49      | 100.38     | 100.87     | 100.56     | 99.80      | 100.00     |
| S/Fe  | 1.97       | 2.00       | 2.01       | 2.01       | 2.01       | 2.01       |
| Co/Ni | 5.76       | 2.17       | 0.99       | 5.99       | 4.39       | 0.48       |

Figure 3. Variations in Co and Ni abundances in pyrites (min; max; average content)

In terms of the rare elements composition, the sampled quartz differs sharply from that in the gold-quartz deposits of South Verkhoianye (Table 2, Figure 4). It has higher contents of Co, W, Sr, Y and, rarely, Cu and Zr. Ni prevails over Co. Quartz from gold deposits of the region is enriched in As and Pb.
Table 2. Abundance of rare and rare-earth elements in quartz of veins from the Upper Carboniferous rocks of South Verkhoyanye, ppm

| Elements | Q-31 | Q-35 | Q-43 | OGD in the southern South Verkhoyanye |
|----------|------|------|------|---------------------------------------|
| As       | 0.55 | 0.39 | 1.77 | 11.47 | 1.55 | 433.69 |
| Sb       | 0.11 | 1.49 | 0.51 | 1.14  | 0.56 | 6.23  |
| Co       | 133  | 72.68| 147  | 1.06  | 0.066| 0.89  |
| Ni       | 1.4  | 1.19 | 3.7  | 4.30  | 3.27 | 5.11  |
| Sn       | 1    | 0.54 | 0.13 | 0.33  | 0.19 | 0.32  |
| W        | 1540 | 915  | 1636 | 107.36| 4.41 | 4.73  |
| Pb       | 1.38 | 0.49 | 3.34 | 1298.45| 5.00 | 6.73  |
| Bi       | 0.028| 0.01 | 0.007| 2.73  | 0.073| 0.053 |
| Mo       | 0.16 | 0.14 | 0.3  | 8.92  | 6.65 | 8.34  |
| Ag       | 0.03 | 0.11 | 0.05 | 2.47  | 0.05 | 0.08  |
| Cu       | 9.23 | 7.85 | 20.92| 9.85  | 13.68| 4.01  |
| Sr       | 589  | 1074 | 900  | 2.75  | 6.60 | <0.001|
| Rb       | 0.13 | 0.15 | 0.99 | 0.45  | 0.032| 0.28  |
| Cs       | 0.02 | 0.03 | 0.07 | 0.019 | 0.01 | 0.029 |
| Be       | 0.008| 0.004| 0.013| 0.018 | 0.008| 0.009 |
| Y        | 8.37 | 4.53 | 13.34| 0.10  | 0.048| 0.002 |
| Zr       | 0.41 | 0.47 | 1.69 | 0.62  | 0.26 | 0.12  |
| Nb       | 0.05 | 0.06 | 0.16 | 0.27  | 0.16 | 0.09  |
| Ta       | 0.19 | 0.19 | 0.22 | 0.004 | <0.001| <0.001|
| La       | 0.421| 0.639| 2.277| 0.088 | 0.017| 0.016 |
| Ce       | 1.213| 1.490| 5.488| 0.185 | 0.038| 0.036 |
| Pr       | 0.182| 0.202| 0.701| 0.032 | 0.004| 0.004 |
| Nd       | 0.936| 0.946| 3.036| 0.085 | 0.012| 0.017 |
| Sm       | 0.444| 0.436| 0.967| 0.022 | 0.002| 0.003 |
| Eu       | 0.386| 0.810| 0.558| 0.004 | 0.001<0.001 |
| Gd       | 0.878| 0.705| 1.638| 0.020 | 0.005| 0.002 |
| Tb       | 0.198| 0.131| 0.336| 0.003 | 0.009<0.001 |
| Dy       | 1.399| 0.754| 2.253| 0.021 | 0.007<0.001 |
| Ho       | 0.297| 0.130| 0.474| 0.004 | <0.001<0.001 |
| Er       | 0.885| 0.340| 1.349| 0.009 | 0.005<0.001 |
| Tm       | 0.131| 0.045| 0.183| 0.001 | <0.001<0.001 |
| Yb       | 0.869| 0.281| 1.090| 0.010 | 0.005<0.001 |
| Lu       | 0.120| 0.032| 0.142| 0.001 | <0.001<0.001 |
| Co/Ni    | 95.00| 61.08| 39.73| 0.25  | 0.02 | 0.17  |
Figure 4. Rare elements distribution in quartz from veins in the northern South Verkhoyanye (Q) and from veins of OGD (Duet, Yur, Nekur) in the southern South Verkhoyanye.

The REE abundance in the studied quartz grains is an order of magnitude higher than in chondrites, and varies within a wide range (19.60 to 314.76 ppm). This parameter distinguishes it from hydrothermal quartz of gold deposits in South Verkhoyanye, which is depleted in rare and rare-earth elements (Figure 5).

Figure 5. REE distribution in quartz from veins in the northern South Verkhoyanye (Q) and from veins of OGD (Duet, Yur, Nekur) in the southern South Verkhoyanye.

The results of isotope studies showed that $\delta^{34}$S values in pyrite vary within narrow limits (-2.5…–2.7‰, (n=6), rarely ranging up to -7.1‰.

Quartz is characterized by isotopically heavy oxygen ($\delta^{18}$O=18.1…–21.8‰, n=10) in contrast to quartz from gold ore deposits in South Verkhoyanye ($\delta^{18}$O=13.9…–15.3‰; n=10, Nezhdaninskoye deposit; $\delta^{18}$O=14.2…–15.3‰, n=5, Lazurnoye deposit [6]).
The results of the mineralogical-geochemical analysis of mineralization in the Upper Carboniferous terrigenous rocks provide better constraints on its formation conditions and typomorphic features.

Microscopic observations showed that metasomatic pyrite occurs as cubic crystals 0.5 to 2.0 mm in size. Electron microprobe analysis revealed the presence in pyrite of trace elements such as Co, Ni, Sb and, rarely, As, Cu, and Zn. The total amount of trace elements averages 0.1-0.3%, occasionally ranging up to 3.0%. 50% of the studied pyrite grains contain excessive sulfur, which is characteristic of metasomatic pyrite. Co and Ni contents vary widely (Co=0.03-1.5%; Ni=0.01-0.5%). This suggests the presence of both diagenetic and metamorphogenic-hydrothermal pyrite in the samples.

The precision LA-ICP-MS analysis showed that the quartz grains under study contain a wide range of trace elements varying greatly in concentration. The largest variations are observed for As, Co, W, Pb, Mo, Sr, and Y concentrations in metamorphogenic and hydrothermal quartz. This reflects specific conditions of different mineral-formation stages. Metamorphogenic quartz has some peculiarities in REE distribution which may be considered typomorphic. The quartz grains exhibit an Eu anomaly serving as an indicator of redox conditions of ore deposition. In metamorphogenic quartz, the Eu anomaly is positive (Eu/Eu* =1.25-3.1), while hydrothermal quartz of OGD is characterized by slightly negative values (Eu/Eu* =0.63-0.84). The obtained Eu/Eu* values indicate a change of oxidizing conditions to reducing ones, and are considered to be a typomorphic feature of metamorphogenic quartz.

3. Conclusions
The data presented here indicate that sulfide mineralization hosted in the Upper Carboniferous rocks in South Verkhoyanye bears evidence of both diagenetic and hydrothermal origin. Clearly defined redox conditions favored the enrichment of the sediments in ore elements. The primary sulfidized sediments were subsequently acted upon by metamorphogenic-hydrothermal solutions, which resulted in the formation of polysulfide sphalerite-galena-chalcopyrite association. Pyrite is characterized by the presence of trace amounts of Co, Ni, Sb and, rarely, As, Cu and Zn. The value of the Co-Ni index ranges within 0.1-2.0, which is typical of metamorphogenic-hydrothermal pyrite. Metamorphogenic quartz exhibits a number of special features that distinguish it from hydrothermal quartz. Its REE content far exceeds that of hydrothermal auriferous quartz from gold deposits in the region. It is also marked by a heavy oxygen isotopic composition and by the prevalence of Ni over Co.

Typomorphic features of the metamorphogenic mineralization need to be studied in more detail to be used as criteria of potential productivity of mineralization in the Upper Carboniferous rocks of South Verkhoyanye.

Acknowledgements
The work was conducted as part of the Russian State Assignment Project of DPMGI SB RAS and was partially financially supported by the Russian Foundation for Basic Research, grant no. 18-45-140040 r_a.

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