

Article

Cu and Au Mineralization of the Tolparovo Ore Occurrence: Evidence for the Formation of Redbed Copper Occurrences in Neoproterozoic Deposits of the Southern Urals

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Abstract: The mineralization and geochemical features of the Tolparovo ore occurrence are studied to reveal the contribution of diagenetic and epigenetic processes in the formation of copper mineralization in redbed deposits. The methods of electron microscopy, ICP MS, X-ray fluorescence, X-ray phase, atomic absorption, thermogravimetric analyses, and C and O isotopic composition were used. The ore is confined to the fault zone and feathering dolomite–calcite veins, having formed at temperatures of ~330–200 °C and pressures of 0.8–0.2 kbar. Similar to other copper redbed occurrences of the Bashkirian uplift, the Tolparovo copper ore occurrence is confined to basal Neoproterozoic deposits. Siliciclastic and carbonate deposits of this level were accumulated at low paleoequator latitudes in arid climates of continental and coastal–marine environments close to evaporite ones. Rocks of this stratigraphic interval demonstrate increased background concentrations of copper (~2–5 times exceeding the clark), which explains the stratification of redbed copper ore occurrences, indicating a predominantly sedimentary copper source. However, most of the redbed copper ore occurrences of the Bashkirian uplift are located in tectonic zones and are associated with the dikes of the Inzer gabbrodolerite complex. This connects the generation of ore occurrences with the formation of the Southern Urals Arsha Large Igneous Province (707–732 Ma) and the activity of postmagmatic fluids. Magmatic processes were presumably activated due to the collapse of the Rodinia supercontinent. It is shown that copper mineralization in stratiform deposits may result from a joint manifestation of dia- and epigenesis processes.

Keywords: sediment-hosted stratiform copper deposits; redbed copper ore occurrences; Neoproterozoic; Southern Urals; copper sulfides; native gold; tellurides



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1. Introduction

The western slope of the Southern Urals is recognized as a promising region for the search and detection of copper in industrial concentrations [1–7]. Numerous magmatic (Cu–Ni, Cu–Ti–Fe), volcanogenic–hydrothermal (Cu–porphyry), and hydrothermal–metamorphogenic (Cu–sulfide) small deposits and ore occurrences of copper, known in this region, are located mainly in the central part of the Bashkirian uplift. Here, they form a wide strip in the submeridional and northeastern direction (Figure 1a, deposits and ore occurrences are indicated by numbers 1–23). In the vast majority of cases, the deposits are spatially and genetically related to various heterochronous magmatic complexes, localized in Mesoproterozoic deposits [4].

At the same time, in the western part of the Bashkirian uplift (Inzer synclinorium and Alatau anticlinorium), stratiform ore occurrences of copper have been found in Neoproterozoic redbed deposits (see Figure 1a,b, ore occurrences are indicated by numbers 24–27,29), which are referred to as sedimentary–diagenetic formations [2,4,5]. At present, stratiform copper deposits play an important economic role [8–11]. They contain about 20% of the

world's copper reserves [12]. One significant group of stratiform deposits is represented by the so-called redbed copper deposits, which are widely represented globally [13–21].

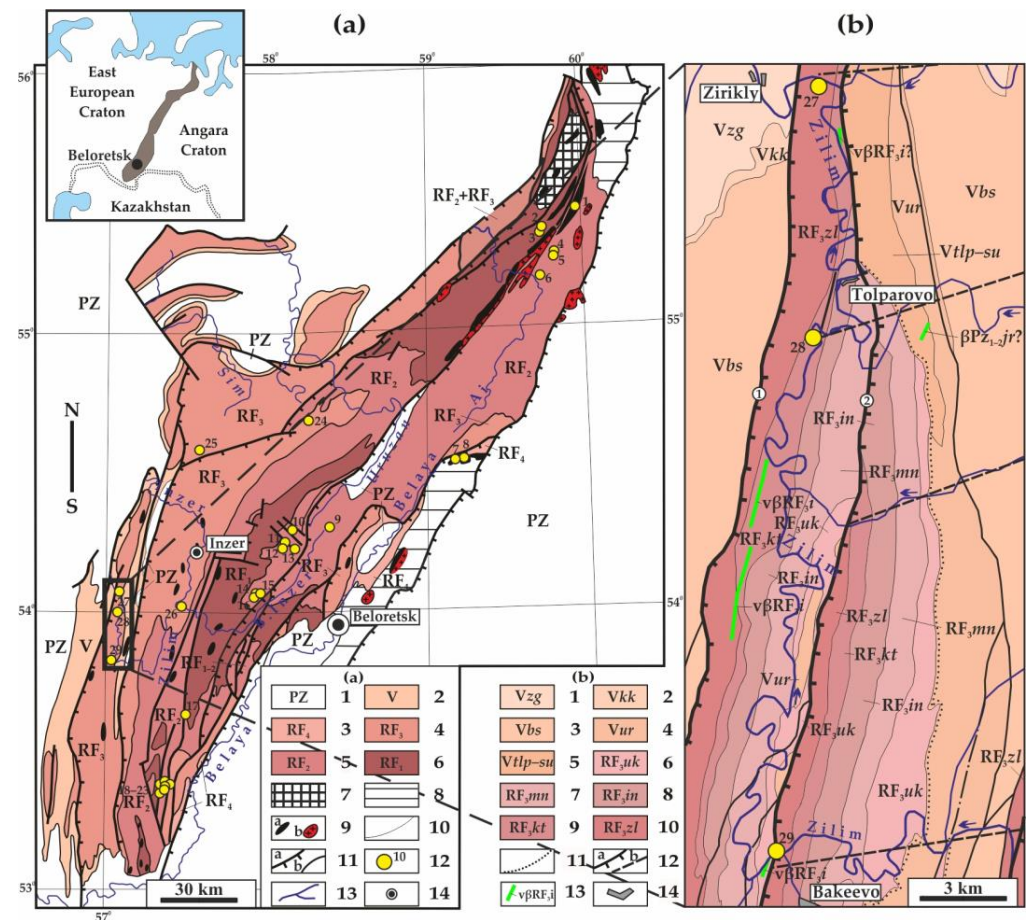


Figure 1. (a) Schematic geological map of the Bashkirian uplift according to ([22]) and (b) a fragment of the Alatau anticlinorium geological map (according to [23] with additions) with the location of copper deposits and ore occurrences (according to [1,2,5,6,24–26] and materials of the West Bashkirian complex geological expedition). Legend. For the map (a): 1–6—undivided deposits: 1—Paleozoic (PZ), 2—Vend (V), 3—final (RF₄), 4—upper (RF₃), 5—middle (RF₂), 6—lower (RF₁) Riphean; 7—Taratash metamorphic complex; 8—Uraltau and Ufaley metamorphic complexes; 9—igneous rocks: gabbro (a) and granites (b); 10—geological boundaries; 11—main tectonic disturbances: a—thrusts; b—faults; 12—copper deposits and ore occurrences (1—Fofanovka, 2—Andreevka, 3—Nikolaevka, 4—Evgrafovka, 5—Nadezhdinka, 6—Urenga, 7—Barsinka, 8—Kiryabinka, 9—Medvezhka, 10—Kazavda, 11—Yamantau, 12—Kuzelga, 13—Kalpak, 14—Kaintyube, 15—Vasilyevskaya Polyana, 16—Arepkulovo, 17—Bogryashka, 18—Aktash-1, 19—Bezmyannoye, 20—Aktash-2, 21—Bolshye Polyany, 22—Yuzhny Aktash, 23—Berezovye kashi, 24—Katav, 25—Lemesa, 26—Bolshoy Inzer, 27—Zirikly, 28—Tolparovo, 29—Bakeevo); 13—rivers; 14—settlements. For the map (b): 1–5—Vendian deposits, formations: 1—zigan (Vzg), 2—kukkarauk (Vkk), 3—basa (Vbs), 4—uryuk (Vur), 5—undivided tolparovo and suirovo (Vtlp-su); 6–10—Upper Riphean deposits, formations: 6—uk (RF_{3uk}), 7—minyar (RF_{3mn}), 8—inzer (RF_{3in}), 9—katav (RF_{3kt}), 10—zilmerdak (RF_{3zl}); 11—boundary of deposit disconformity; 12—tectonic disturbances: a—thrusts (1—Avdyrdak-Alatau, 2—Western Kalinsk), b—probable; 13—gabbrodolerite dikes (vβRF_{3i}—Inzer complex, βPz_{1-2jr}—Yurmaty complex); 14—settlements.

Despite the relatively low concentrations of Cu (<1.0 wt %), the redbed copper ore occurrences of the Bashkirian uplift are promising in terms of identifying industrial copper deposits on the western slope of the Southern Urals, where large-scale mineralization

is predicted [6,7]. The copper–sulfide mineralization here is confined to the Zilmerdak and Katav formations (Figure 2) with an age of approximately ~1000–800 Ma according to [27–29]. The deposits of the formations have a characteristic red color due to the presence of diagenetic hematite and magnetite [30,31].

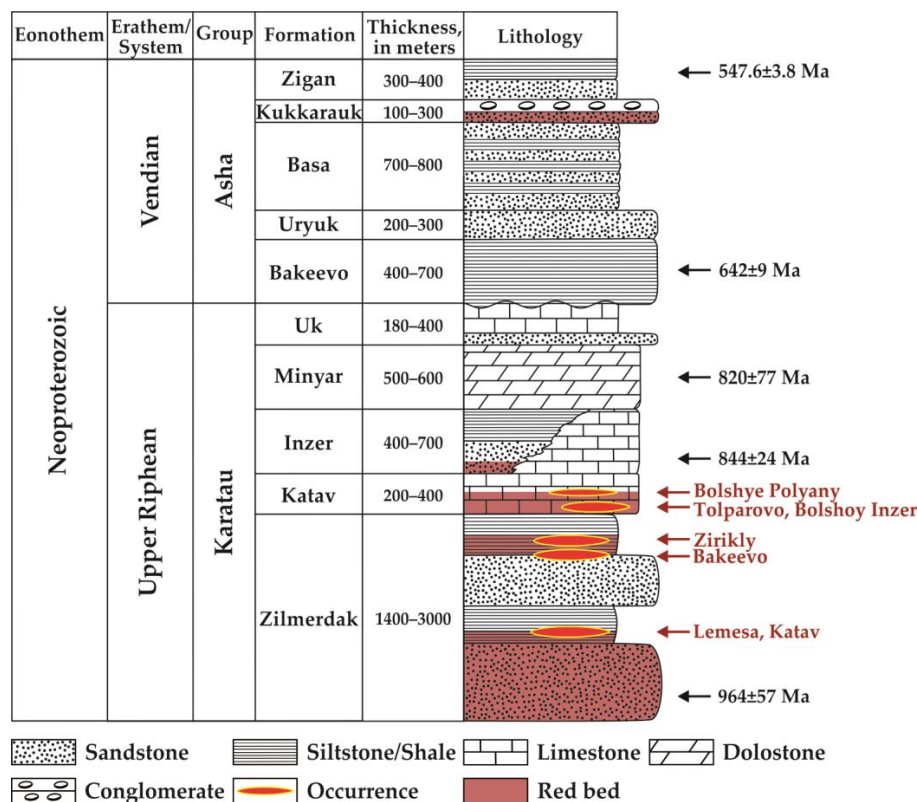


Figure 2. Generalized stratigraphic column of Neoproterozoic strata of the Southern Urals according to [22,32] with current geochronological constraints and locations of redbed copper occurrences. Geochronological data are provided according to [27,28,33,34].

However, no consensus has been reached so far on the time of copper sulfide formation in the stratiform deposits (whether it is diagenetic or epigenetic), as well as on the duration of the sulfide formation processes [35–40]. For example, the genesis of copper belt deposits in Central Africa remains controversial. Some researchers believe [18,41,42] the copper sulfides in these deposits to have formed at the stage of diagenesis; hence, their age comprises ~800 Ma and is consistent with the age of host dolomitic shales, formed in evaporite depositional environments. Other researchers claim [43,44] that disseminated and vein mineralization in the copper deposits of Central Africa has an epigenetic nature, having formed in the synorogenic time from 609 to 473 Ma. However, the existence of an earlier syndiagenetic copper mineralization remains possible. In the Dongchuan Copper Deposits of Southern China, studies [45,46] found that the mineralization of copper in the Paleoproterozoic host rocks was non-diagenetic despite its formation ~780–700 Ma ago in connection with the pulses of magmatic activity during the collapse of the Rodinia supercontinent. At the same time, according to [47], the time of the copper–sulfide mineral formation in Southern China deposits comprised ~1700 Ma and was close to the age of its hosting dolostones (1742 ± 13 Ma). It is widely believed that copper mineralization in stratiform deposits is multistage and is due to the implementation of various geological processes throughout the sedimentary–tectonic evolution of host basins [8,9,13,36,38,42–44,48,49].

To date, no detailed mineralogical studies of redbed copper ore occurrences on the western slope of the Southern Urals have been carried out. The works [2,5–7] provide only a macroscopic description of the ore mineralization in the Katav and Lemesa ore occurrences

of the Zilmerdak formation. Meanwhile, in 2022–2023, in the Alatau anticlinorium near the Tolparovo village, we found a new ore occurrence of copper in the redbed limestones of the Katav formation (see Figure 1a,b, the ore occurrence is indicated by the number 28). In this study, we analyze the geological, mineralogical, and geochemical features of the Tolparovo ore occurrence, as well as other redbed copper ore occurrences in the western slope of the Southern Urals. The aim was to identify the participation of diagenetic or epigenetic processes in the formation or transformation of the copper mineralization on the basis of mineralogical and geochemical indicators, as well as to determine the conditions of its formation in the Neoproterozoic redbed deposits of the Alatau anticlinorium.

2. Geological Setting

The Alatau anticlinorium is located in the western part of the Bashkirian uplift. It covers an area of about 240 km × 25 km. The western and eastern borders of the anticlinorium pass along the Alatau and Zilmerdak thrusts, respectively. It consists of three overthrusts, moving upon each other from the east, with a thickness varying from 1–2 to 3–4 km and an output width ranging from 4 to 12 km [50]. Accordingly, from west to east, a threefold repetition of a stratigraphic sequence for the anticlinorium sedimentary section is recorded in general terms. The overthrust boundaries include the Avdyrdak-Alatau and Western Kalinsk submeridional thrusts (see Figure 1b). In their frontal parts, a significant deformation of rocks is noted with an extensive formation of steep anticlinal folds and tectonic faults [50]. The anticlinorium is divided into a series of submeridionally elongated anticlines (Avdyrdak, Alatau, etc.) and synclines (Yashkurt, Kulgunino, etc.) [51].

Neoproterozoic deposits of the Alatau anticlinorium are represented by the Karatau and Asha series, whose ages are approximately ~1000–540 Ma (see Figure 2) [27,28,33,34]. The Karatau series includes the Zilmerdak, Katav, Inzer, Minyar, and Uk formations [22,52]. The Zilmerdak formation, which is the basal formation for the Karatau series, unites (from below) the Biryán, Nugush, Lemesa, and Bederysh subformations [52]. Redbed sandstones with interlayers of gravelstones, conglomerates, and rare subordinate layers of siltstones, mudstones, and dolostones prevail in the Biryán subformation. The Nugush subformation is composed of sandstones, siltstones, mudstones, and clay dolostones. The Lemesa subformation is represented by light gray sandstones with subordinate layers of siltstones and mudstones. The Bederysh subformation is composed of sandstones, siltstones, mudstones, and clay dolostones. The rocks of the Nugush and Bederysh subformations in the lower part are red and red-brown, and in the upper part—light and green-gray [2,5,6]. The Katav formation is composed of red, red-brown (lower subformation), and gray (upper subformation) clay limestones [22,52]. The Inzer formation is represented by sandstones, siltstones, limestones, and mudstones. The Minyar formation is composed of dark gray, gray dolostones, and dolomitic limestones with chert interlayers and lenses in the upper part. The Uk formation is represented by sandstones with stromatolites, limestones, siltstones, and mudstones.

The magmatic formations of the Alatau anticlinorium are represented by gabbrodolerite dikes of the Inzer complex [50,51]. According to [51], the U–Pb age of the Inzer complex comprises 721 ± 6.9 Ma. The gabbrodolerite dikes are spatially biased to the Avdyrdak-Alatau and Western Kalinsk thrusts, where they break through the deposits of the Zilmerdak and Katav formations (see Figure 1b). Dikes can be traced along the strike for 6–7 km. In addition, thin dikes of gabbrodolerites, secant to the Uryuk formation deposits, are rarely observed in the anticlinorium (see Figure 1b). The geochronological data for these dikes are absent. They can be presumably attributed to the Jurmatin Early-Middle Paleozoic complex [23,50].

The Tolparovo ore occurrence is located in the southern part of the Avdyrdak anticline on the left bank of the river Zilim, ~1.5 km south-west of Tolparovo village (see Figure 1b). Here, red-brown and light gray, fine- and medium-laminated, micrograined clay limestones of the Katav formation are exposed (Figure 3a–g). The rocks are contorted into a synclinal fold (see Figure 3b). The rock stratification of its southeastern and northwestern limbs is

inclined to the south–west ($207\text{--}244^\circ \angle 27\text{--}73^\circ$) and to the east ($65\text{--}95^\circ \angle 35\text{--}80^\circ$), respectively, with a dip azimuth of the fold bend and dip angle equal to $145\text{--}150^\circ$ and 20° , respectively.

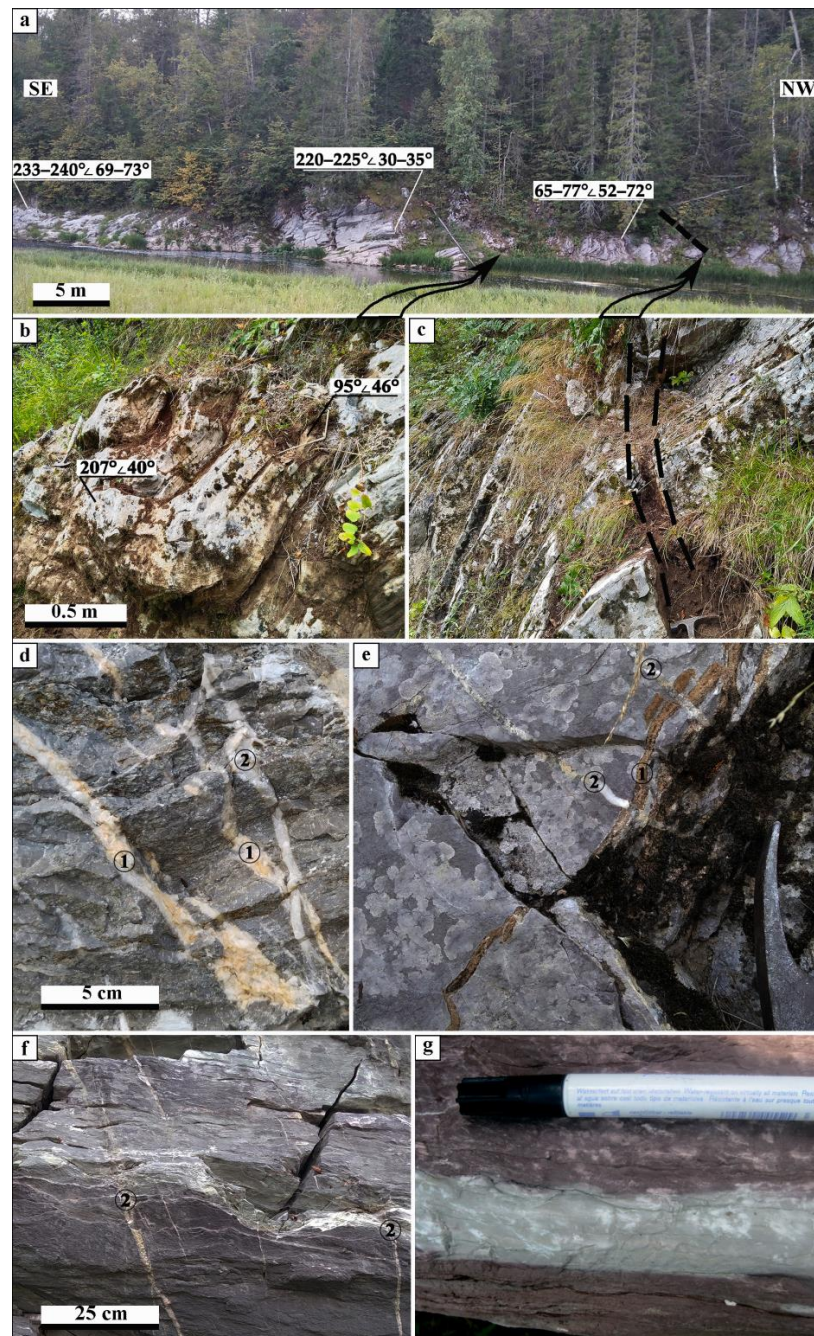


Figure 3. Geological conditions of gray and red limestones of the Katav formation on the left bank of the river Zilim ~1.5 km south–west of Tolparovo village, location of the mineralized ore zone and the relationship of mineralized dolomite–calcite veins with late barren calcite veins. Legend: (a)—general view of the exposure; arrows show the fold bend and reverse fault (dashed line) locations in the section; (b)—synclinal fold bend; (c)—dashed lines denote the zone of the mineralized postfold low-amplitude reverse fault in the northwestern limb of the synclinal fold; (d,e)—relationship of mineralized dolomite–calcite veins, filling shear fractures ((d), number 1 in circles) and tension joints ((e), number 1 in circles), complementary to the reverse fault, with late barren milky-white calcite veins ((d,e), number 2 in circles) in gray (d) and red (e) layers; (f)—late barren calcite veins in redbed limestone (number 2 in circles); (g)—red and gray subordinated layers in limestones.

In the limestones of the northwestern limb near the fold bend, a postfolded low-amplitude reverse fault is observed with the fault plane inclined to the west by $265\text{--}283^\circ$ at an angle of $64\text{--}67^\circ$ (see Figure 3c). The mineralized fault zone with a width of $\sim 12\text{--}20$ cm is filled with poorly cemented, ferruginated, brecciated, boudinaged fragments of dolomite–calcite rocks with slickensides. The reverse fault is feathered by low-thick ($0.5\text{--}2.5$ cm) yellow–brown, frequently ferruginated, mineralized ore dolomite–calcite veins, filling fault-associated shear fractures ($275\text{--}288^\circ \angle 50\text{--}80^\circ$, see Figure 3d) and tension joints ($170\text{--}215^\circ \angle 46\text{--}85^\circ$, see Figure 3e).

In addition, late barren milky-white calcite veins, secant for both brecciated rocks in the fault zone and feathering dolomite–calcite veins, are formed in the exposure (see Figure 3d–f). Here, they have a zonal distribution and are most often found in the southeastern limb of the fold near the bend in an area about 15 m long. In this section part, their thickness reaches 10 cm with a length of several meters. In other parts of the section, late calcite veins are observed less often with their thicknesses not exceeding $0.3\text{--}1.0$ cm. The bedding elements of late calcite veins in various limbs of the fold are similar: their dip azimuth in the southeastern limb equals $296\text{--}348^\circ$ with a dip angle of $39\text{--}70^\circ$; in the northwestern limb, these values comprise $298\text{--}334^\circ$ and $28\text{--}50^\circ$, respectively. This indicates a postfold formation of late calcite veins.

The mineralized ore reverse fault zone is traced in the submeridional direction along the azimuth of $10\text{--}15^\circ$ for a distance of about 2.5 km (see Figure 1b). A low-amplitude reverse fault was recorded [22] north of the considered ore occurrence in the section of the Katav formation near Tolparovo village with a vertical displacement amplitude of the fault wall equal to ~ 3 m. Although no detailed geochemical study of this section was performed, single samples of limestones also revealed increased Cu content (up to 0.04 wt %).

3. Materials and Methods

A total of 95 samples were selected from the Katav formation, including 61 samples directly from the Tolparovo ore occurrence and 34 samples from Katav limestones at a considerable distance therefrom. In the ore occurrence, samples were taken from host rocks (24 samples), fault zone (17 samples), mineralized ore dolomite–calcite veins (14 samples), and late barren calcite veins (6 samples). The concentrations of petrogenic oxides and rare elements in rocks and veins (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO , CaO , MgO , Na_2O , K_2O , S_{total} , P_2O_5 , V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Ba) were determined by X-ray fluorescence analysis using an spectrometer XRF (X-Calibur, Xenometrix LTD., Migdal HaEmek, Israel) (Ag-anode, $15\text{--}50$ kV, $60\text{--}1000$ mA). Calibration curves were constructed using state reference materials of limestones (KN, KN-2, KN-3, OSO No. 469-11), dolomitic limestones (SI-2), and dolomites (SI-1, SI-3). The detection limit while measuring petrogenic oxides and rare elements was $0.01\text{--}0.2$ wt % and $3\text{--}10$ g/t, respectively.

The concentrations of Au, Pb, and As were determined by atomic absorption analysis using a Persee A3 spectrometer (PG General Instrument Co., Beijing, China). In order to concentrate and isolate gold from interfering elements, it was extracted with butyl acetate from a hydrochloric acid solution (1/7) at an aqueous to organic phase ratio of 10:1. The concentration of As was determined using a WHG-630 A hydride generator (Xi'an Yima Optoelec Co., Ltd., Xi'an, China). The detection limit in the measurement of Au, Pb, and As comprised 0.2 ppm.

The FeO concentration of bulk samples was established by the volumetric bichromatic titrimetric method. In addition, the fluorine content was determined in the Katav formation samples by the photometric method through the formation of lanthanum fluoride alizarin complexonate according to a procedure described in [53]. Measurements were carried out using a KFK-3-01 photometer (Zagorsk Optical-Mechanical Plant, Sergiyev Posad, Russia) with two state reference materials in each single measurement at a detection limit of 0.005 wt %.

In addition, for determining the copper background concentration in the rocks of the Alatau anticlinorium, samples were taken from Zilmerdak (48 samples), Inzer (34 samples),

Minyar (18 samples), and Uk (5 samples) formations. The concentrations of Cu in the rocks of these formations were determined by X-ray fluorescence analysis.

The mineralogical composition of rocks and veins was determined by thermogravimetric and X-ray diffraction analyses ($n = 35$). Differential thermal analysis was performed by analyst T.I. Chernikova using a Q-1500 derivatograph (MOM, Budapest, Hungary) through heating in air from 20 to 1000 °C at a rate of 10 °C/min. The sample mass was about 500 mg. Radiographic studies were carried out by analyst G.S. Sitdikova using a DRON-4 diffractometer in powder samples with a mass of 0.5–1 g. The analysis was performed in Cu K α radiation (40 kV, 40 mA) in a 2 Θ region of 4–60° with a step of 0.02° and a counting time equal to 10 s.

The composition study of minerals in the host limestones ($n = 4$) and veins ($n = 5$) of the ore occurrence was carried out in polished thin sections by analyst S.S. Kovalev using a Tescan electron microscope (Vega 4 Compact, Tescan Brno s.r.o., Brno, Czech Republic) equipped with an Explorer 15 energy dispersion analyzer (Oxford Instruments, Oxford, UK). Spectra were processed automatically in the AzTec One software package using the TrueQ procedure (version 5.1, Oxford Instruments, Oxford, UK). During the analysis, the following parameters were used: an acceleration voltage of 20 kV, a probe current of 4 nA, 60 s spectrum point accumulation time in the Point&ID mode, a beam diameter of ~3 μ m.

Determination of trace and rare earth elements (REE) (Li, Be, Sc, V, Cr, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Tl, Pb, Bi, Th, U) in host limestones ($n = 3$) and veins ($n = 6$) was carried out at the Institute of Problems of Microelectronics Technology and Highly Pure Materials (Chernogolovka, Russia, Analytical Group Head V.K. Karandashev) by mass spectrometry with inductively coupled plasma using an X-7 mass spectrometer (Thermo Electron Corporation, Warwickshire, UK). The resulting patterns for REE were normalized against NASC [54]. In addition, the ICP MS method was applied to analyze two samples of an insoluble residue after treating the samples with cold 5% HCl for 16 h.

The isotopic composition of C and O in six ore vein samples was determined at the Geoscience Center of the Institute of Geology of the Komi Scientific Center UB RAS (Syktyvkar, Group Head V.L., Andreichev). The digestion of samples to CO₂ in orthophosphoric acid at a temperature of 80 °C and the measurement of the isotopic composition of C and O in the continuous helium flow mode was carried out using an analytical complex, including the Gas Bench II sample preparation and introduction system, connected to a DELTA V Advantage mass spectrometer (Thermo Scientific, Karlsruhe, Germany). International reference materials NBS18 and NBS19 were used for calibration. The measurement reproducibility of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ was within ± 0.2 ‰.

4. Results

4.1. Geochemistry

4.1.1. Trace Elements

The average chemical compositions and average contents of trace elements in the host limestones and veins of the Tolparovo ore occurrence, as well as in the background limestones of the Katav formation, located outside the ore occurrence, according to the results of an X-ray fluorescence and atomic absorption analysis, are given in Table 1. The most significant variations in the chemical composition and distribution of trace elements are characteristic of rocks from the fault zone. In addition, they have the highest concentrations of copper, ranging from 97 to 2981 ppm. In dolomite–calcite veins, filling shear fractures, copper concentrations vary from 35 to 193 ppm, while, for tension joints, this value ranges across 31 to 134 ppm. Late milky-white calcite veins are characterized by the lowest concentrations of copper, from 4 to 22 ppm.

Table 1. Average chemical compositions (wt %) and average concentrations of trace elements (ppm) in the host limestones and veins of the Tolparovo ore occurrence, as well as in the background limestones of the Katav formation outside the ore occurrence.

Oxide, Element	1 (n = 34)	2 (n = 24)	3 (n = 17)	4 (n = 9)	5 (n = 5)	6 (n = 6)
SiO ₂	10.96	10.24	14.33	6.95	4.32	3.72
TiO ₂	0.15	0.12	0.41	0.08	0.08	0.04
Al ₂ O ₃	2.59	2.01	5.24	1.57	1.14	0.86
FeO	0.29	0.32	0.26	0.39	0.33	0.25
Fe ₂ O ₃	0.96	0.71	3.14	0.29	2.15	0.15
MnO	0.04	0.04	0.37	0.05	0.38	0.04
CaO	46.45	47.42	39.23	48.76	48.57	52.11
MgO	1.00	1.47	3.00	1.72	2.74	1.06
Na ₂ O	0.36	0.31	0.24	0.27	0.21	0.16
K ₂ O	0.64	0.33	1.30	0.21	0.18	0.09
P ₂ O ₅	0.07	0.06	0.06	0.05	0.04	0.04
S _{total}	0.02	0.03	0.04	0.03	0.02	0.02
IIIIII	36.41	37.17	32.05	39.33	40.30	40.96
Σ	99.92	100.23	99.65	99.69	100.42	99.52
F	248	203	478	532	315	281
V	21	18	65	23	30	25
Cr	24	11	37	15	13	24
Co	3	3	8	3	10	4
Ni	11	24	18	18	20	12
Cu	19	12	1427	122	81	8
Zn	18	10	24	10	10	7
As	0.6	0.1	15	0.4	0.2	1
Rb	19	16	28	12	11	10
Sr	115	125	65	135	92	140
Y	9	7	9	5	6	4
Zr	41	46	43	38	31	29
Ba	132	68	336	116	413	188
Au	–	<0.2	0.4	0.5	<0.2	<0.2
Pb	3	2	8	2	0.1	4

1—background limestones of the Katav formation outside the Tolparovo ore occurrence; 2–6—Tolparovo ore occurrence: 2—host limestones; 3—mineralized reverse fault zone; 4–5—mineralized dolomite–calcite veins, filling shear fractures (4) and tension joints (5), complementary to the reverse fault; 6—late barren milky-white calcite veins. *n*—number of samples. Dash—n/a.

Copper in the ore occurrence reveals weakly expressed positive geochemical relationships with Si, Ti, Al, Fe, Mn, K, V, Cr, Ni, As, Rb, Au, and Pb (Figure 4). The coefficients of correlation with these elements are at the level of 0.2–0.4. The absence of a positive relationship between the copper and sulfur contents is explained by the development of supergenic processes in the ore occurrence and the replacement of sulfides with copper carbonates. Significant correlation coefficients (~0.5) are demonstrated by copper only with mg and Ba in mineralized dolomite–calcite veins. Along with these elements, the content of Fe, Mn, V, and Ni increases noticeably in the veins that fill tension joints. Host limestones near the veins are similarly enriched in mg.

Au contents of the host rocks are below 0.2 ppm. In rocks of the fault zone and dolomite–calcite veins from shear fractures, the average gold concentrations comprise 0.4–0.5 ppm (see Table 1). In mineralized veins, Au forms weak positive geochemical relationships only with Cu and As with correlation coefficients of ~0.3–0.4.

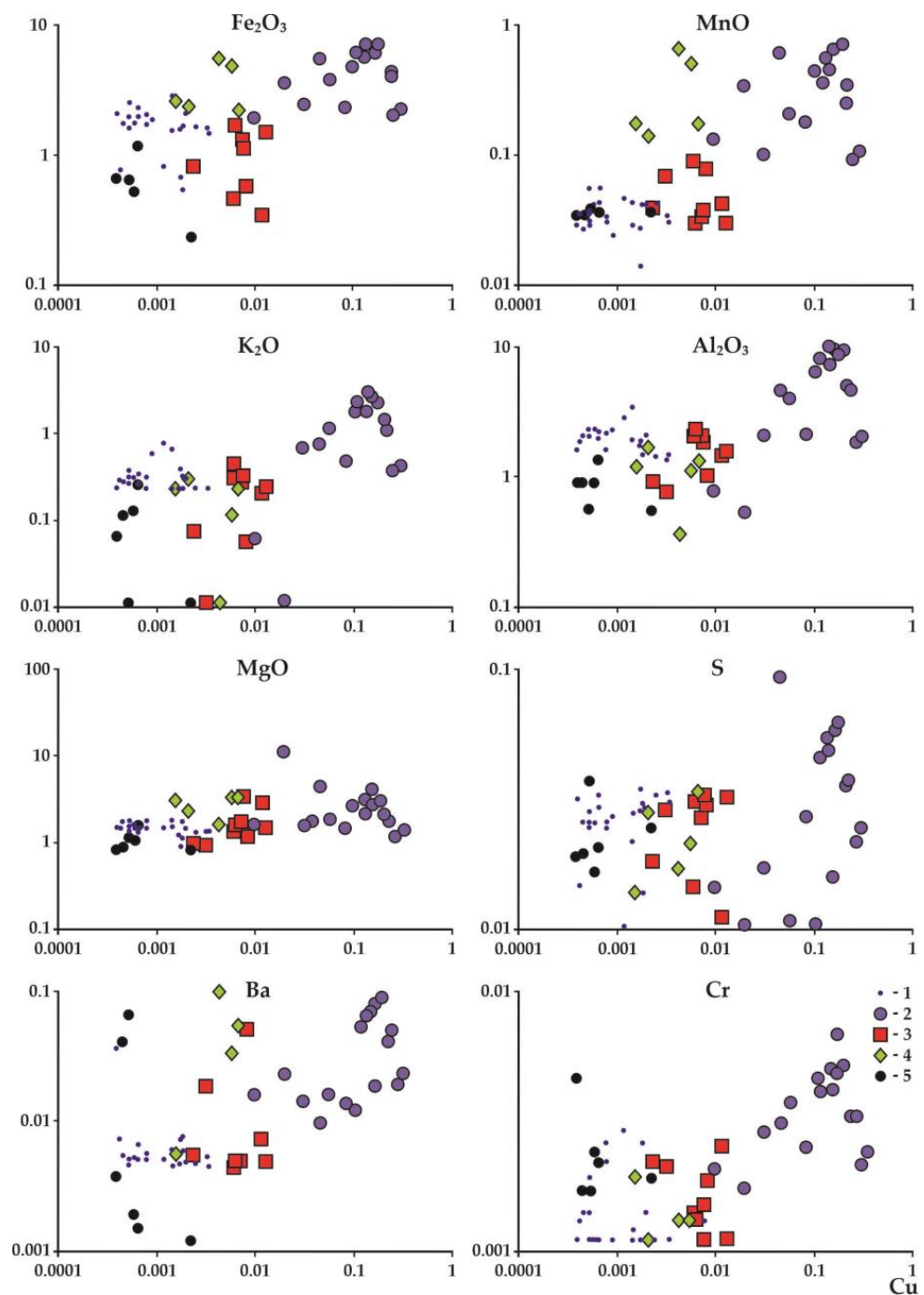


Figure 4. Geochemical relationships between the contents of Cu (wt %) and Fe_2O_3 , MnO, K_2O , Al_2O_3 , mgO, S, Ba, and Cr (wt %) in the Tolparovo ore occurrence. Legend: 1—host limestones; 2—mineralized reverse fault zone; 3—4—mineralized dolomite–calcite veins, filling shear fractures (3) and tension joints (4), complementary to the reverse fault; 5—late barren milky-white calcite veins.

The results of an X-ray fluorescence analysis were generally consistent with the ICP MS data of the mineralized dolomite–calcite veins (Table 2). In the veins, concentrations of V, Co, Ni, As, Se, Rb, Cs, Ba, Tl, Bi, and U increase significantly compared with the “background” limestones of the Katav formation. At the same time, the contents of most elements are similar in dolomite–calcite veins and “background” limestones. The concentration of REE in dolomite–calcite veins is equal to ~25 ppm. This is even slightly lower than in the “background” limestones of the Katav formation with a REE concentration of ~35 ppm.

Table 2. Average concentrations of trace elements (ppm) in the limestones of the Katav formation and mineralized dolomite–calcite veins of the Tolparovo ore occurrence.

Element	1 (<i>n</i> = 3)	2 (<i>n</i> = 3)	3 (<i>n</i> = 3)	4 (<i>n</i> = 1)	5 (<i>n</i> = 1)
Li	6.36	4.16	3.12	50.20	30.40
Be	0.99	0.25	0.11	1.60	1.10
Sc	1.93	2.90	1.35	9.30	13.10
V	bdl	8.40	8.32	90.40	80.50
Cr	5.61	7.35	7.21	70.90	70.15
Co	3.03	7.14	4.16	19.10	13.35
Ni	10.61	81.60	59.74	40.40	31.65
Cu	1.65	92.70	61.80	600.60	600.30
Zn	22.98	13.26	11.44	130.15	110.20
Ga	1.38	1.62	1.80	21.35	18.10
As	bdl	0.85	0.96	10.70	9.60
Se	bdl	0.51	0.05	0.41	0.48
Rb	0.34	10.20	8.32	77.60	80.50
Sr	231.36	171.70	103.00	18.20	40.10
Y	7.67	5.05	5.15	8.30	9.40
Zr	12.10	8.16	11.44	130.10	110.70
Nb	0.98	0.17	0.55	14.10	11.15
Mo	bdl	0.07	0.12	0.80	1.20
Ag	0.02	0.07	0.06	0.74	0.57
Cd	0.10	0.04	0.02	0.19	0.15
Sn	0.36	0.27	0.27	3.00	2.70
Sb	0.24	0.09	0.10	1.30	1.00
Te	bdl	0.02	0.01	0.13	0.06
Cs	0.03	0.31	0.32	3.70	3.20
Ba	11.02	28.56	206.00	131.70	2003.20
La	7.84	5.10	6.12	5.15	8.10
Ce	13.20	9.18	10.20	6.20	11.30
Pr	1.57	1.20	1.10	0.65	1.05
Nd	6.33	5.10	5.20	2.10	3.50
Sm	1.27	1.00	1.05	0.50	0.70
Eu	0.24	0.19	0.20	0.21	2.40
Gd	1.24	0.86	0.92	0.62	1.10
Tb	0.19	0.13	0.12	0.14	0.15
Dy	1.10	0.70	0.61	1.20	1.20
Ho	0.22	0.15	0.14	0.31	0.30
Er	0.67	0.42	0.35	1.10	1.10
Tm	0.09	0.06	0.05	0.19	0.18
Yb	0.56	0.40	0.35	1.40	1.30
Lu	0.09	0.06	0.05	0.22	0.21
Hf	0.43	0.23	0.27	4.15	4.05
Ta	0.07	0.00	0.03	1.00	0.80
W	0.17	0.03	0.19	2.60	1.90
Tl	0.01	0.03	0.05	0.50	0.50
Pb	1.95	4.08	1.05	9.00	2.00
Bi	0.02	0.09	0.06	0.90	0.60
Th	1.17	0.90	0.92	7.05	9.15
U	0.21	1.10	0.41	5.20	2.10

1—host limestones; 2–3—mineralized dolomite–calcite veins, filling shear fractures (2) and tension joints (3); 4–5—insoluble residue of dolomite–calcite veins, filling shear fractures (4) and tension joints (5); *n*—number of samples; bdl—below detection limit.

4.1.2. Isotopic Composition of C and O

In mineralized dolomite–calcite veins, the $\delta^{13}\text{C}$ comprises 1.2–1.8‰ (VPDB), while $\delta^{18}\text{O}$ ranges from −8.4 to −8.0 ‰ (VPDB) (Table 3). The carbon and oxygen isotopic compositions of the veins vary within very narrow limits and have a weak negative correlation with each other ($K_{\text{corr}} = -0.38$).

Table 3. Isotopic composition of C and O (‰, VPDB) in mineralized dolomite–calcite veins of the Tolparovo ore occurrence.

	Sample No.					
	b8	m2612a	m2620	m3059	m3062	m3063
$\delta^{13}\text{C}$	1.5	1.8	1.7	1.3	1.2	1.3
$\delta^{18}\text{O}$	−8.3	−8.4	−8.2	−8.4	−8.2	−8.0

4.2. Mineralogy

4.2.1. Host Rocks

The content of calcite in the host limestones of the Katav formation averages 81–86% (Table 4). In variable amounts from 1 to 8%, quartz, muscovite, albite, chlorite, and hematite are present in the rocks. For host rocks, extremely low contents of dolomite and K-feldspar are typical, averaging less than 1% and being, in most cases, below the detection limit of thermogravimetric and X-ray diffraction analyses.

Table 4. Average mineralogical compositions of Katav formation background limestones, as well as host rocks and veins of the Tolparovo ore occurrence.

Mineral	1 (<i>n</i> = 21)	2 (<i>n</i> = 5)	3 (<i>n</i> = 4)	4 (<i>n</i> = 3)	5 (<i>n</i> = 2)
Calcite	81	86	68	77	68
Dolomite	<1	<1	10	6	19
Quartz	8	5	6	6	2
Muscovite	3	2	7	4	5
Chlorite	3	3	5	4	3
Albite	3	2	2	2	1
K-feldspar	<1	<1	1	<1	<1
Hematite	1	<1	<1	<1	<1

1—background limestones of the Katav formation outside the Tolparovo ore occurrence; 2–5—Tolparovo ore occurrence: 2—host limestones; 3—mineralized reverse fault zone; 4–5—mineralized dolomite–calcite veins, filling shear fractures (4) and tension joints (5), complementary to the reverse fault; *n*—number of samples.

4.2.2. Ore Veins

In the ore occurrence, calcite, quartz, muscovite, albite, chlorite, and hematite are also the main forming minerals of rocks from the fault zone and their feathering ore veins. However, in contrast to the host rocks, these rocks are associated with significant dolomite contents, averaging 6–19% (see Table 4). Vein dolomite is more frequently represented by individual rhombohedral crystals and their segregations, and less often by vein-shaped secretions. Generally, dolomite in veins can be associated with chlorite and ore minerals (Figure 5a,b). The content of mgO and FeO in vein calcite varies from 0.21 to 0.53 and 0.14 to 0.33 wt %, respectively, with the MnO concentration reaching 0.19 wt %. In the dolomite of ore dolomite–calcite veins, the concentrations of FeO and MnO comprise 0.35–5.20 and 0.15–0.50 wt %, respectively.

Vein chlorite forms “pedate” precipitations near the rhombohedral crystals of dolomite and copper sulfides (see Figure 5a,b,i). The chemical composition of chlorite mainly corresponds to pycnochlorite and diabantite in single analytical procedures (Table 5, Figure 6). Chlorites are characterized by slight fluctuations in iron content with *x*(Fe) values ranging within 0.32–0.37.

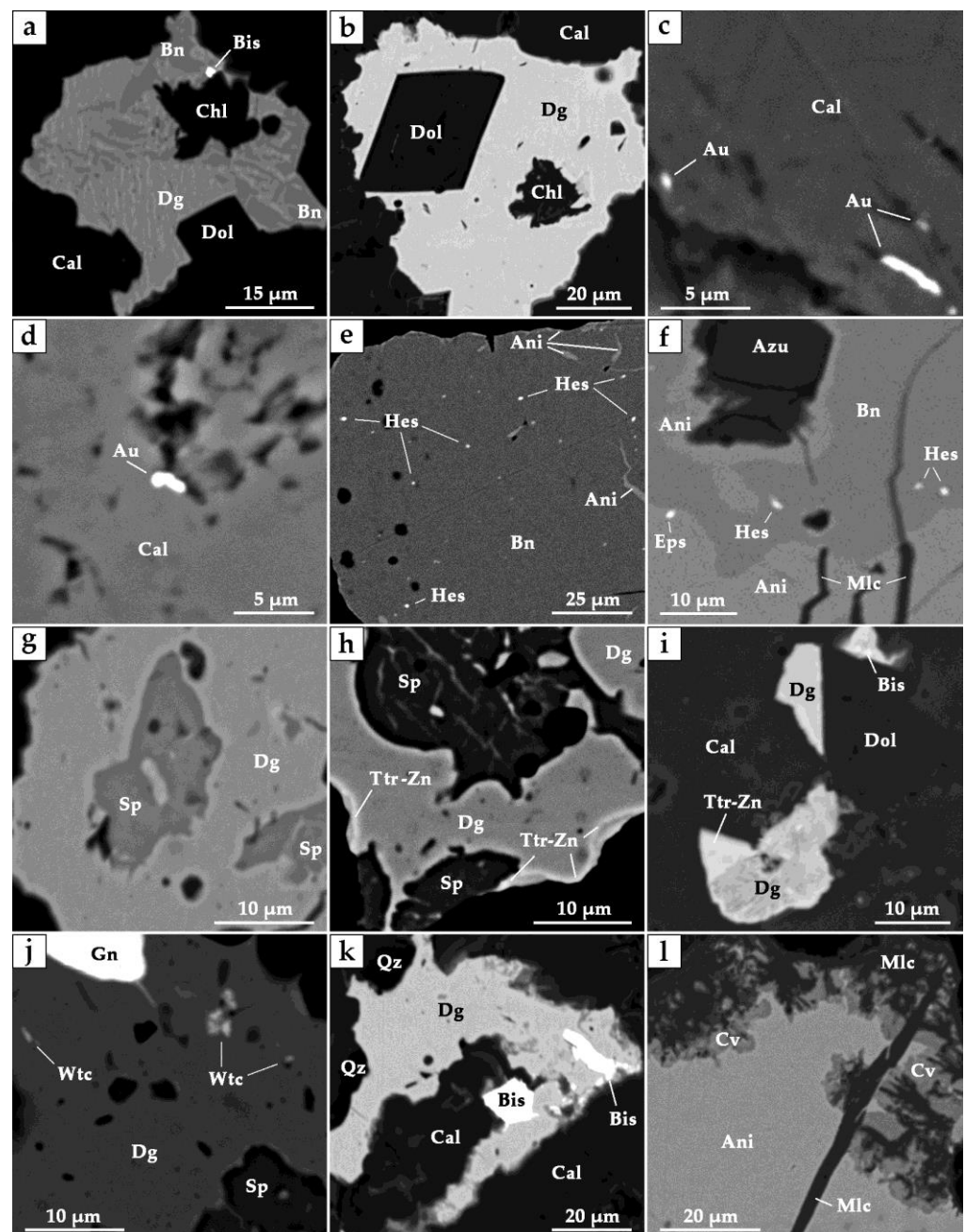


Figure 5. BSE-images of minerals from the dolomite–calcite veins of the Tolparovo ore occurrence. Legend: (a)—micrographic texture of the bornite and digenite intergrowth in association with dolomite and chlorite; (b)—digenite in association with dolomite and chlorite; (c,d)—secretions of native gold; (e)—inclusions of hessite in bornite; bornite is substituted by anilite along the fractures; (f)—inclusions of hessite and empressite in bornite; bornite is substituted by anilite, azurite, and malachite; (g)—intergrowth of digenite and sphalerite; (h)—disseminated texture of digenite and sphalerite intergrowth; secretions of tetrahedrite-(Zn) in digenite at the sphalerite boundary; (i)—intergrowth of digenite and tetrahedrite-(Zn); (j)—inclusions of galena and wittichenite in digenite, digenite and sphalerite intergrowths; (k)—inclusions of bismite in digenite, digenite associated with quartz; (l)—bornite is substituted with anilite, covellite, and malachite. Ani—anilite; Au—native gold; Azu—azurite; Bis—bismite; Bn—bornite; Cal—calcite; Chl—chlorite; Cv—covellite; Dg—digenite; Dol—dolomite; Eps—empressite; Gn—galena; Hes—hessite; Mlc—malachite; Qz—quartz; Sp—sphalerite; Ttr-Zn—tetrahedrite-(Zn); Wtc—wittichenite.

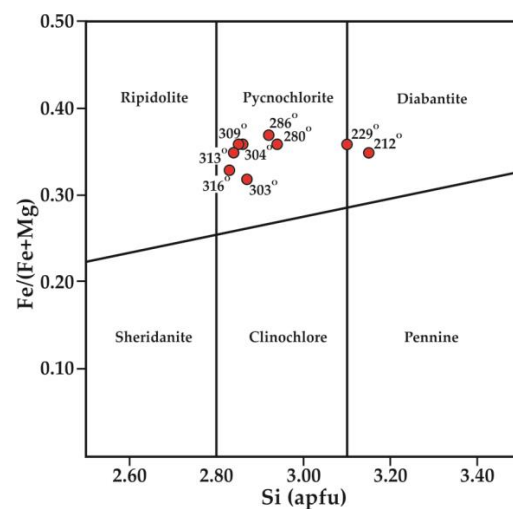


Figure 6. Chlorite composition on the classification diagram of [56]. Numbers show the formation temperatures calculated using a chlorite geothermometer [55] (Table 5).

Table 5. Chemical composition of chlorite (wt %) and calculated temperatures of its formation.

	Grain No.								
	1	2	3	4	5	6	7	8	9
SiO ₂	27.30	28.00	27.17	27.92	27.34	27.38	30.07	29.40	27.74
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.17	0.00
Al ₂ O ₃	21.80	21.53	21.64	20.73	22.27	21.59	21.31	19.61	21.40
Cr ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FeO	18.21	17.66	18.19	19.30	17.83	17.17	16.99	17.97	16.35
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	17.95	17.86	17.83	18.06	18.74	19.98	17.55	17.56	19.75
CaO	0.39	0.45	0.87	0.27	0.00	0.00	0.00	0.00	0.39
Na ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.30	0.24
Total	85.65	85.55	85.70	86.28	86.18	86.12	85.92	86.01	85.87
Crystallochemical coefficients in the chlorite formula (calculation for 20 cations)									
Si	5.73	5.88	5.70	5.84	5.67	5.65	6.30	6.19	5.74
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.19	0.00
Al	5.39	5.33	5.35	5.11	5.45	5.25	5.26	4.87	5.21
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe ^{III}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe ^{II}	3.19	3.09	3.19	3.37	3.09	2.96	2.97	3.16	2.82
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	5.61	5.59	5.57	5.63	5.79	6.14	5.47	5.51	6.08
Ca	0.09	0.10	0.20	0.06	0.00	0.00	0.00	0.00	0.09
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.08	0.06
x(Mg)	0.64	0.64	0.64	0.63	0.65	0.67	0.65	0.64	0.68
Al(IV)	2.27	2.12	2.30	2.16	2.33	2.35	1.70	1.81	2.26
Al(VI)	3.12	3.21	3.05	2.95	3.12	2.90	3.56	3.06	2.95
x(Fe)	0.36	0.36	0.36	0.37	0.35	0.33	0.35	0.36	0.32
T, °C	304	280	309	286	313	316	212	229	303

In calculating the crystallochemical formula, Al(IV) supplements Si position to 8 cations and Al(VI) accounts for the remaining part of the total calculated amount of Al. The temperatures were calculated using a chlorite geothermometer [55].

Barite in dolomite–calcite veins is found in the form of xenomorphic secretions and crystals of a rectangular cross-section up to 80 µm in size, often in association with quartz. In the chemical composition of barite, up to 1.62 wt % of Sr impurity is recorded.

Ore mineralization in the veins is represented by chalcopyrite, pyrite, native gold, bornite, digenite, sphalerite, galena, tetrahedrite-(Zn), wittichenite, hessite, empressite, bismite, anilite, geerite, covellite, azurite, malachite, and barite. Chalcopyrite and pyrite form a rare thin dissemination in dolomite–calcite veins from a system of shear fractures. The size of the chalcopyrite secretions is 3–60 μm , and cubic pyrite crystals reach 0.5 mm in size. Cu (up to 1.72 wt %) and Co (up to 0.45 wt %) impurities are observed in pyrite (Table 6). In one case, an Mo impurity (2.37 wt %) was found in the chalcopyrite.

Table 6. Chemical composition of iron, copper, and bismuth sulfides (wt %).

Mineral	Pyrite	Chalcopyrite	Bornite	Digenite	Anilite	Geerite	Covellite	Wittichenite
<i>n</i>	7	15	15	35	20	4	12	9
Chemical composition of minerals (wt %)								
Cu	1.19	33.38	62.94	77.93	76.44	74.78	67.06	38.76
Fe	46.61	30.43	10.00	0.01	0.11	0.43	0.05	bdl
Co	0.11	Bdl	bdl	Bdl	bdl	bdl	bdl	bdl
Bi	bdl	Bdl	bdl	Bdl	bdl	bdl	bdl	42.59
S	51.96	35.42	26.25	21.73	22.71	23.71	31.79	19.29
Total	99.76	99.23	99.19	99.67	99.21	98.89	98.90	100.63
Crystallochemical coefficients in the minerals formula (a.p.f.u)								
Cu	0.02	0.97	4.98	9.02	6.92	7.95	1.03	3.02
Fe	1.01	1.00	0.90	0.00	0.01	0.05	0.00	0.00
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bi	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.01
S	1.96	2.03	4.12	4.98	4.07	5.00	0.97	2.97
Cu/S	–	–	–	1.81	1.70	1.59	1.06	–

bdl—below detection limit, *n*—number of analyses.

In dolomite–calcite veins, native gold is associated with pyrite and chalcopyrite. Gold is found in calcite in the form of isometric and lamellar secretions with a size of 1–5 μm (Figure 5c,d). The composition of gold includes significant and variable amounts of copper (35.45–51.69 wt %), a small amount of silver (4.11–5.08 wt %), and often an impurity of zinc (0.64–1.19 wt %) (Table 7). The chemical composition of gold is variable. It varies from an almost stoichiometric composition of auricuprid $\text{Cu}_{3.02}(\text{Au}_{0.84}\text{Ag}_{0.14})_{0.98}$ to Cu-containing gold $(\text{Cu}_{3.07}\text{Zn}_{0.05})_{3.12}(\text{Au}_{1.65}\text{Ag}_{0.23})_{1.88}$ and $(\text{Cu}_{1.96}\text{Zn}_{0.06})_{2.02}(\text{Au}_{0.84}\text{Ag}_{0.14})_{0.98}$.

Table 7. Chemical composition of native gold and silver tellurides (wt %).

Sample No.							
<i>n</i>	b8-1	b8-2	b8-3	b8-4	m2609-1	m2609-2	m2609-3
	3	3	1	2	4	6	2
Chemical composition of minerals (wt %)							
Au	58.99	53.64	53.22	44.66	bdl	bdl	bdl
Ag	4.43	4.78	5.08	4.11	62.60	61.20	41.20
Cu	35.45	40.42	39.85	51.69	bdl	bdl	bdl
Zn	0.64	0.97	1.19	bdl	bdl	bdl	bdl
Te	bdl	bdl	bdl	bdl	37.70	37.81	57.54
Total	99.50	99.82	99.34	100.45	100.30	99.01	98.74
Crystallochemical coefficients in the minerals formula (a.p.f.u)							
Au	1.65	0.84	0.84	0.84	0.00	0.00	0.00
Ag	0.23	0.14	0.15	0.14	1.99	1.97	0.92
Cu	3.07	1.97	1.95	3.02	0.00	0.00	0.00
Zn	0.05	0.05	0.06	0.00	0.00	0.00	0.00
Te	0.00	0.00	0.00	0.00	1.01	1.03	1.08

bdl—below detection limit, *n*—number of analyses.

Bornite stands out both in the form of independent grains and in the form of intergrowths with digenite. The size of bornite grains ranges from $5\ \mu\text{m} \times 15\ \mu\text{m}$ to $150\ \mu\text{m} \times 300\ \mu\text{m}$. In polished sections, their typical shape is elongated without clear boundaries and with large parallelogram grains. Intergrowths of bornite and digenite form micrographic (myrmecite) textures (see Figure 5a), which indicate the simultaneous formation of these minerals. The typical size of bornite–digenite secretions of an isometric or slightly elongated rectangular shape is $50\text{--}70\ \mu\text{m}$. In the chemical composition of bornite ($\text{Cu}_{4.98}\text{Fe}_{0.90}\text{S}_{4.12}$), a slight iron deficiency and some excess sulfur contents are recorded (see Table 6).

Bornite contain numerous small ($2\text{--}3\ \mu\text{m}$) inclusions of silver tellurides—mainly hessite and, less often, empressite (see Figure 5e,f). The chemical composition of hessite ($\text{Ag}_{1.97\text{--}1.99}\text{Te}_{1.01\text{--}1.03}$) does not significantly deviate from the stoichiometric composition of this mineral (see Table 7). In empressite ($\text{Ag}_{0.92}\text{Te}_{1.08}$), a slight excess of tellurium is observed (see Table 7).

Digenite is most common in the ore veins of copper sulfides. In addition to micrographic intergrowths with bornite, it forms disseminating intergrowths with sphalerite (see Figure 5g,h,j), as well as independent secretions up to $70\ \mu\text{m}$ in size (see Figure 5b,k). In digenite, associated with sphalerite, tetrahedrite-(Zn) secretions (see Figure 5h,i), galena, and small ($1\text{--}3\ \mu\text{m}$) inclusions of wittichenite (see Figure 5j) are noted. In many cases, isometric or xenomorphic bismite secretions up to $20\ \mu\text{m}$ in size are noted along the edges of digenite grains (see Figure 5i,k). The ratio of copper and sulfur (1.81) in digenite ($\text{Cu}_{9.02}\text{S}_{4.98}$) is close to stoichiometric (see Table 6). Rarely, an insignificant impurity of Fe, reaching 0.13 wt %, is noted in this copper sulfide.

Sphalerite is established only in intergrowths with digenite. Small isometric inclusions of galena are sometimes noted in sphalerite. Various grains of sphalerite exhibit minor variations in the chemical composition ($\text{Zn}_{0.96\text{--}0.98}\text{Cu}_{0.01\text{--}0.02}\text{Fe}_{0.00\text{--}0.01}\text{S}_{1.00\text{--}1.03}$), which corresponds to the almost ideal stoichiometric composition of this mineral (Table 8). Sphalerite is characterized by a low Fe content (0.18–0.45 wt %) and relatively high Cu concentrations (0.50–1.07 wt %).

Table 8. Chemical composition of sphalerite (wt %).

	Grain No.									
	1	2	3	4	5	6	7	8	9	10
Zn	65.27	64.43	64.51	65.44	65.68	65.42	66.34	64.70	65.33	66.01
Fe	0.21	0.45	0.20	0.29	0.20	0.29	0.20	0.18	0.33	0.28
Cu	0.50	0.87	0.81	0.80	0.82	0.80	0.75	1.07	0.83	0.68
S	34.65	33.15	32.93	33.59	33.53	33.58	34.49	33.08	33.07	33.17
Total	100.63	98.90	98.45	100.12	100.23	100.09	100.78	99.03	99.56	100.14
Crystallochemical coefficients in the minerals formula (a.p.f.u)										
Zn	0.96	0.97	0.97	0.97	0.98	0.97	0.98	0.97	0.98	0.98
Fe	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.01	0.01
Cu	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01
S	1.03	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.00	1.00
FeS, mol %	0.36	0.79	0.35	0.50	0.35	0.50	0.34	0.32	0.57	0.49
CuS, mol %	0.76	1.35	1.25	1.22	1.25	1.22	1.14	1.65	1.28	1.04

Tetrahedrite-(Zn) forms thin ($1\text{--}2\ \mu\text{m}$) coronas in digenite (see Figure 5h) and intergrowths with this mineral along smooth boundaries (see Figure 5i). Tetrahedrite-(Zn) has a variable chemical composition (Table 9). Fluctuations are noted in the content of Zn (5.46–8.84 wt %), As (9.64–13.87 wt %), Sb (9.61–14.55 wt %), and Bi, which is found in relatively high concentrations (1.34–2.25 wt %) only in some tetrahedrites-(Zn). Fe concentrations vary slightly from 0.52 to 0.70 wt %. The As/(As + Sb) ratio ranges within 0.40–0.57, compared with Zn/Fe ranging within 9.84–12.91 (see Table 9).

Table 9. Chemical composition of tetrahedrite-(Zn) (wt %).

	Grain No.									
	1	2	3	4	5	6	7	8	9	10
Cu	41.65	42.34	41.57	43.74	42.78	41.30	42.26	41.16	41.21	38.89
Zn	5.69	6.10	5.80	5.46	6.64	6.66	6.89	6.89	7.23	8.84
Fe	0.53	0.56	0.54	0.52	0.61	0.54	0.70	0.58	0.56	0.70
As	12.59	11.50	13.05	11.92	13.61	9.86	13.87	10.84	9.64	11.02
Sb	9.61	10.08	11.20	10.56	10.30	13.40	10.30	13.87	14.55	14.28
Bi	2.03	2.25	1.34	1.77	bdl	bdl	bdl	bdl	bdl	bdl
S	25.95	26.86	26.91	27.26	27.17	26.77	26.86	26.39	26.96	25.42
Total	98.05	99.69	100.41	101.23	101.11	98.53	100.88	99.73	100.15	99.15
Crystallochemical coefficients in the minerals formula (a.p.f.u)(calculation for 29 atoms)										
Cu	10.46	10.42	10.18	10.59	10.28	10.25	10.20	10.18	10.12	9.77
Zn	1.39	1.46	1.38	1.28	1.55	1.61	1.62	1.66	1.73	2.16
Fe	0.15	0.16	0.15	0.14	0.17	0.15	0.19	0.16	0.16	0.20
As	2.68	2.40	2.71	2.45	2.77	2.08	2.84	2.27	2.01	2.35
Sb	1.26	1.29	1.43	1.33	1.29	1.74	1.30	1.79	1.86	1.87
Bi	0.15	0.17	0.10	0.13	0.00	0.00	0.00	0.00	0.00	0.00
S	12.91	13.10	13.05	13.08	12.94	13.17	12.85	12.94	13.12	12.65
As/(As + Sb)	0.57	0.53	0.54	0.53	0.57	0.42	0.57	0.44	0.40	0.44
ln(Zn/Fe)	2.38	2.39	2.36	2.36	2.39	2.51	2.29	2.48	2.56	2.54

bdl—below detection limit.

Wittichenite occurs as inclusions (1–3 μm) in both independent grains of digenite and in digenite–sphalerite associations (see Figure 5j). The chemical composition of wittichenite ($\text{Cu}_{3.02}\text{Bi}_{1.01}\text{S}_{2.97}$) is close to the stoichiometric one (see Table 6).

Anilite typically forms after bornite in association with azurite and malachite (see Figure 5f,l). Individual small (up to 20 μm) xenomorphic grains, completely composed of anilite, are less common. In the chemical composition of anilite ($\text{Cu}_{6.92}\text{Fe}_{0.01}\text{S}_{4.07}$), as well as in bornite, a slight iron deficiency and some excess sulfur contents are recorded. Accordingly, the ratio of copper and sulfur (1.70) in this mineral is less than in stoichiometric anilite (see Table 6). In anilite, up to 0.27 wt % of an Fe impurity is sometimes recorded.

Geerite and covellite typically form after anilite in association with azurite and malachite (see Figure 5k,l). Geerite corresponds to an almost ideal stoichiometric composition ($\text{Cu}_{7.95}\text{Fe}_{0.05}\text{S}_{5.00}$) with a Cu/S ratio of 1.59 (see Table 6). Covellite ($\text{Cu}_{1.03}\text{S}_{0.97}$) forms skeletons around malachite secretions. Impurities of Fe up to 1.28 and up to 0.14 wt % are occasionally noted in geerite and covellite, respectively.

5. Discussion

5.1. Reconstruction of Physico-Chemical Parameters of Ore Formation

5.1.1. Calcite, Dolomite, and Chlorite

According to the distribution of mgO , FeO , and MnO in the dolomites and calcites from ore veins, it is possible to calculate the temperatures and pressures of their formation using a geothermobarometer [57]. The calculation of the temperature and pressure is carried out according to the formulas $\text{mg}'_{\text{Cal}} = \text{mg}_{\text{Cal}}(1 + 11.5\text{Fe}_{\text{Cal}} + 5\text{Fe}_{\text{Cal}}^2 + 550\text{Fe}_{\text{Cal}}^3 + 8\text{Mn}_{\text{Cal}} - 50\text{Mn}_{\text{Cal}}^2)$, $C_{\text{Fe}} = \text{Fe}_{\text{Cal}}/(\text{Fe}_{\text{Dol}} + \text{Mn}_{\text{Dol}})$, where mg_{Cal} , Fe_{Cal} , Fe_{Dol} , Mn_{Cal} , and Mn_{Dol} are mole fractions of mg , Fe , and Mn in calcite and dolomite. Using this geothermobarometer, e.g., for gold deposits of the Southern Urals [58], demonstrates a good correspondence between the calculated formation temperatures of dolomite–calcite veins and the homogenization temperatures of their fluid inclusions. The calculated values of the temperature and pressure for dolomite–calcite paragenesis formation in the Tolparovo ore occurrence comprise 198–330 $^{\circ}\text{C}$ and 0.2–0.8 Kbar (20–80 MPa), respectively (Figure 7). These temperatures agree well with the temperatures of chlorite formation, ranging between 212 and 316 $^{\circ}\text{C}$ and calculated using a chlorite thermometer [55].

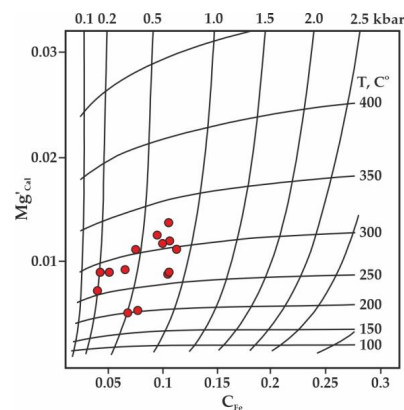


Figure 7. Composition of dolomite–calcite paragenesis in mineralized veins of the Tolparovo ore occurrence on the dolomite–calcite geothermobarometer diagram according to [57].

5.1.2. Pyrite, Chalcopyrite, and Native Gold

In the ore occurrence, the native gold of the dolomite–calcite veins associates with pyrite and chalcopyrite. In the Au–Cu–Ag diagram (Figure 8a), the figurative points of the chemical composition for the auricuprid of the Tolparovo ore occurrence are located near the liquidus isotherm of 300 °C, and the figurative points of other gold compounds are about 400 °C. The mutual solubility of the components in solid solutions of Au–Cu–Ag decreases with a temperature drop from 700 to 350 °C [59]. At a temperature of <350 °C, the formed gold phases with a low silver or copper content become metastable [60,61]. Experimental studies [62] show that under hypogene conditions with water/rock ratios equal to 200–250, oxidative processes can greatly affect the stability of intermetallic compounds in the Au–Cu–Ag system. Under such conditions, auricuprid decomposes according to the following scheme: $\text{AuCu}_3 \rightarrow \text{AuCu} \rightarrow \text{Au}_3\text{Cu} \rightarrow \text{disordered solid solution} \rightarrow \text{copper oxides}$. According to the published data, summarized in [62], the stability temperature of the cubic and tetragonal auricuprid is more than 390 and 285 °C, respectively. On this basis and the data presented in the diagram (Figure 8a), it can be concluded that the temperature of the auricuprid formation in the Tolparovo ore occurrence and, accordingly, its associated pyrite and chalcopyrite, is not less than 285 °C.

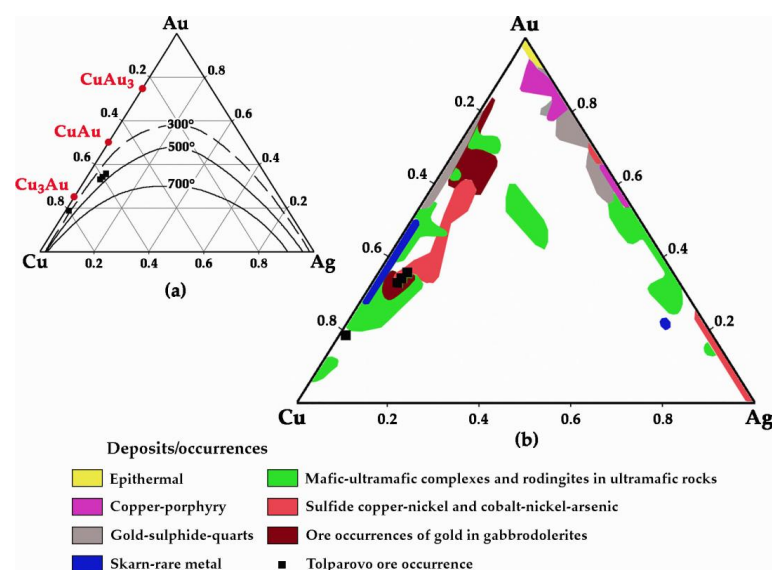


Figure 8. (a) Au–Ag–Cu diagrams with liquidus isotherms (according to [62,63]) and (b) compositions of Cu-containing native gold and silver (at %) from deposits/ore occurrences of various types (compiled according to [64–70]).

5.1.3. Sphalerite, Digenite, and Tetrahedrite-(Zn)

Intergrowths of sphalerite, digenite, and tetrahedrite-(Zn), represented by disseminated textures (see Figure 5h) in the Tolparovo ore occurrence, indicate the conditions of their joint crystallization. It should be noted that the considered mineral association is rather rare in stratiform copper deposits. Here, sphalerite tends to form intergrowths with chalcopyrite and galena, as well as with tennantite, pyrite, and, rarely, with chalcocite [49]. According to these studies, the temperature of the sphalerite–chalcopyrite paragenesis formation ranges between 230 and 350 °C, sometimes reaching up to 400 °C. Despite the sphalerite + digenite association being rare, it was obtained experimentally through a hydrothermal synthesis at a pressure of 1 Kbar and a temperature of 400 °C [71]. In addition, the micrographic intergrowths of bornite, digenite, sphalerite, and galena with high concentrations of gold and silver are described as the main minerals in the deposits of the modern subaerial geothermal system of Reykjanes in Iceland [72]. In this geothermal system, fluids rise from a depth of 2.5 km, having a temperature of 270–315 °C. The precipitation of bornite, digenite, sphalerite, and galena occurs at the outlet of the pipes under the conditions of boiling fluids due to a sharp pressure drop to 22–37 bar at a temperature of about 250 °C.

In order to calculate the temperature of the sphalerite and tetrahedrite-(Zn) formation in the Tolparovo ore occurrence, we used a geothermometer, developed for the paragenesis of permanent sphalerite with the tetrahedrite and tennantite of variable compositions [73]. The authors of the geothermometer assume an isothermal deposition of zonal faded ore, when each successive zone crystallizes under conditions of local osmotic equilibrium, fixed by the distribution of Fe and Zn in sphalerites and tetrahedrites–tennantites. The temperature is calculated according to the equation $T(K) = -((664 \pm 30)/m)$, where $T(K)$ is the kelvin temperature and m is the slope ratio of the regression line for the figurative points of tetrahedritic tennantite compositions on the $As/(As + Sb) - \ln(Zn/Fe)$ diagram [73]. The temperatures for the formation of coexisting sphalerite and tetrahedrite-(Zn) (195–280 °C), calculated using the geothermometer, e.g., for the Teremki gold deposit in the Eastern Transbaikalia, correspond well to the temperatures of the homogenization of fluid inclusions (216–298 °C) in the productive stage quartz [74].

In the dolomite–calcite veins of the Tolparovo ore occurrence with a variable composition of tetrahedrite-(Zn), the Fe content in sphalerite slightly varied from 0.32 to 0.79 mol % FeS (see Table 8). Therefore, we can assume that with the crystallization of sphalerite and coexisting tetrahedrite-(Zn), an osmotic equilibrium of the Fe and Zn exchange was achieved. Between the values of $As/(As + Sb)$ and Zn/Fe ratios in tetrahedrites-(Zn), a significant inverse relationship is recorded with a correlation coefficient equal to -0.85 . The slope ratio of the regression line for the figurative points of tetrahedrite-(Zn) compositions on $As/(As + Sb) - \ln(Zn/Fe)$ diagram equals to -1.222 (Figure 9a) with the calculated temperature of its formation being 270 ± 25 °C.

Taking into account data on the contents of FeS and CuS in sphalerite (see Table 8) and the calculated crystallization temperature of coexisting sphalerite and tetrahedrite-(Zn), it is possible to estimate the fugacity of sulfur in the ore-forming system according to the equation from [75]: $\log_{10} f S_2 = 11.01 - 9.49(1000/K) + [0.187 - 0.252(1000/K)] \times (\text{mol \% FeS in sphalerite}) + [0.35 - 0.2(1000/K)] \times (\text{mol \% CuS in sphalerite})$, where K is the kelvin temperature. In sphalerite of the Tolparovo ore occurrence, a relatively high copper content (0.76–1.65 mol % CuS) (see Table 8) is revealed, which, however, does not exceed its solubility limit. According to the studies in [76], the solubility limit of CuS in sphalerite is 2.4 mol % at temperatures of 300–500 °C without a correlation between the contents of Fe and Cu in sphalerite ($K_{\text{corr}} = 0.02$), which excludes the presence of the microinclusions of chalcopyrite in sphalerite. The calculations carried out using the equation from [75] show that the deposition of sphalerite and tetrahedrite-(Zn) in mineralized veins occur at a high sulfur fugacity, ranging from 10–7.6 to 10–5.8 (Figure 9b).

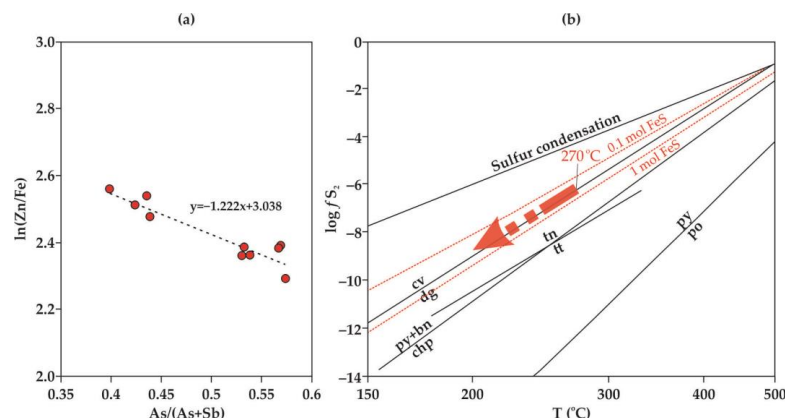


Figure 9. (a) Tetrahedrite-(Zn) composition on the As/(As + Sb)–ln(Zn/Fe) diagram and (b) sulfur fugacity diagram ($\log f_{\text{S}_2}$)—temperature (T °C) (from [73,77]). The dotted line shows the isopleths of FeS content (mol %) in sphalerite. Legend: bn—bornite; cv—covellite; chp—chalcopyrite; dg—digenite; po—pyrrhotite; py—pyrite; tn—tennantite; tt—tetrahedrite.

5.1.4. Hessite, Empressite

According to [78], the temperatures of telluride formation are typically less than 250 °C and do not exceed 350 °C. According to the experimental data and thermodynamic calculations [79,80], hessite and empressite are stable at temperatures below 500 °C (α -Ag₂Te– β -Ag₂Te's phase transformation temperature is about 150 °C) and 192 °C, respectively. Empressite is less common than hessite. Together, these minerals are described, e.g., in the Sandaowanzi epithermal Au–Ag–Te deposit (Aihui District, Heihe, Heilongjiang, China), where they were deposited in the final stages of the hydrothermal process under oxidative conditions at a temperature of about 240 °C [81]. Hessite and empressite were also noted as part of the late gold–telluride–palladium mineralization in the gabbrodolerites of the Pay-Khoy Ridge (Yugorsky Peninsula, Nenets Autonomous Okrug, Russia) [67]. The formation temperature of silver tellurides in this ore occurrence does not exceed 260 °C.

Hessite is generally one of the first formed telluride minerals. For the Fancha gold deposit (Xiaoqinling mining district, Lingbao City, Sanmenxia, Henan, China) and San Luis Alta Au–Ag–Te–(Bi–Se) deposit (Rio Grande district, Condesuyos Province, Arequipa, Peru), this is due to the fact that this mineral requires a relatively low fugacity of Te for its formation [82,83].

The calculated values of the sulfur fugacity during the formation of a sphalerite–digenite–tetrahedrite mineral association allow the tellurium fugacity in the Tolparovo ore occurrence to be estimated. In the diagram $\log f_{\text{S}_2}$ – $\log f_{\text{Te}_2}$ (Figure 10), the hessite stability field, limited by the Au equilibrium line, is located between the tellurium fugacity values of $10^{-10.7}$ and $10^{-7.8}$.

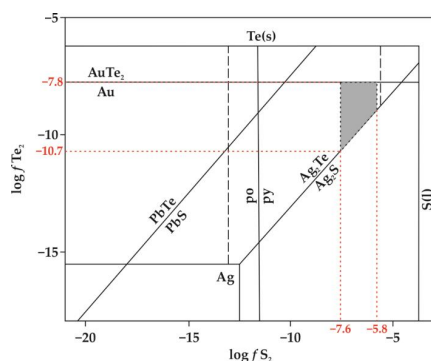


Figure 10. Diagram $\log f_{\text{S}_2}$ – $\log f_{\text{Te}_2}$ at 300 °C (from [84]) and stability field for silver telluride minerals of the Tolparovo ore occurrence.

5.1.5. Sequence of Mineral Formation in the Tolparovo Ore Occurrence

The average temperatures of mineral formation in the Tolparovo ore occurrence according to dolomite–calcite, chlorite, and sphalerite–tetrahedrite geothermometers are $277 \pm 39^\circ$, $284 \pm 38^\circ$, and $270 \pm 25^\circ\text{C}$, respectively. The similarity of temperatures, obtained using three independent geothermometers, indicates the reliability of the values obtained. At the initial stage of mineral formation in the ore-forming system, the pressure reached 0.7–0.8 Kbar (dolomite–calcite geothermobarometer estimates). The formation of ore minerals proceeded with a decrease in temperatures and pressures to $<200^\circ\text{C}$ and 0.2 Kbar, respectively. At this stage, pyrite, chalcopyrite, auricuprid, bornite, digenite, sphalerite, tetrahedrite-(Zn), galena, wittichenite, hessite, and empressite were deposited in association with dolomite, chlorite, and barite (Figure 11). Mineral deposition occurred at a high sulfur fugacity, typical of bornite-containing ores [19,84,85], equal to $10^{-7.6}–10^{-5.8}$. The tellurium fugacity was $10^{-10.7}–10^{-7.8}$. Mineral formation probably occurred with a sequential change in oxidative conditions to alkaline ones. The calculations of the physicochemical parameters of ore formation in stratiform copper deposits show that the deposition of the pyrite $\rightarrow$ chalcopyrite $\rightarrow$ bornite $\rightarrow$ chalcocite association should be accompanied by a change in the pH of the medium from acidic to alkaline [19]. The initial oxidative conditions in the Tolparovo ore occurrence can be indicated by the presence of barite in the mineralized veins, where Cu directly correlates with Ba contents (see Figure 4).

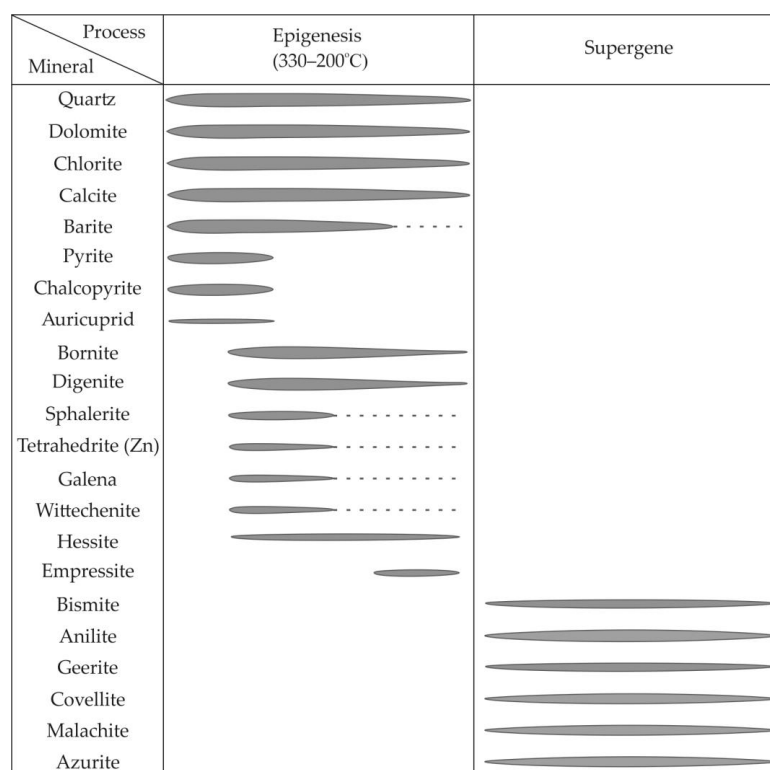


Figure 11. Paragenetic succession of the Tolparovo ore occurrence.

Ore mineralization in dolomite–calcite veins has small sizes, typically not exceeding 0.1 mm and reaching 0.3–0.5 mm in rare cases. This is probably not accidental and may be due to the deposition of minerals from supersaturated solutions under the conditions of an extremely rapid decrease in temperature and pressure. Fast cooling products from supersaturated solutions are typically characterized by fine-grained intergrowths of bornite, digenite, and sphalerite, observed in both hydrothermal experiments [71,85,86] and natural objects [72].

Anilite, geerite, and covellite in the ore occurrence develop in close association with copper carbonates—azurite and malachite (see Figure 5e,f,k,l). All minerals of this asso-

ciation are involved in the substitution of bornite and digenite. High-copper minerals of the chalcocite–digenite series are unstable in an exogenous environment [13,49,85], as referenced in these works. The presence of even a small amount of oxygen in the ore-forming system leads to the oxidation and removal of copper. Experimental studies show that the dissolution of digenite via an acidic solution of iron sulfate leads to the formation of anilite, followed by metastable polymorphs of geerite, spioncopite, yarrowite, and covellite, whose structure is based on the cubic closest packing of sulfur atoms [87]. Anilite is characterized by a low temperature stability $<76\text{ }^{\circ}\text{C}$, while covellite has two stability fields, i.e., $<75\text{ }^{\circ}\text{C}$ and about $507\text{ }^{\circ}\text{C}$ [13,49,85], as referenced in these works. Based on the above materials and the observed textural features, it can be concluded that anilite, geerite, covellite, azurite, and malachite in the Tolparovo ore occurrence formed when bornite and digenite were substituted under hypogene conditions (see Figure 11) at low temperatures and, probably, increased acidity. The formation of bismite also appears to have been associated with supergenic processes. This bismuth oxide may have been formed by the oxidation of wittichenite, included in digenite.

5.2. Sources of Ore Mineralization

5.2.1. REE

The behavior of REE in stratiform copper deposits is used to identify the diagenetic or hydrothermal epigenetic origin of ore minerals, as well as to determine the degree of their epigenetic alterations (for example, [88–90]). The ores of some stratiform copper deposits demonstrate a relationship between the content of Cu and the amount of REE. This is explained either by hydrothermal activity with an REE input (for example, in the Paratoo deposit in South Australia [88]), or by the diagenetic processes of ore mineral formation and their subsequent oxidation (for example, the Kupferschiefer deposit in Poland [89] and the Nahand-Ivand Area deposits in Iran [90]).

In the Tolparovo ore occurrence, the distribution of REE in the dolomite–calcite veins and background limestones of the Katav formation is highly similar (Figure 12a). Both veins and background limestones exhibit the same subhorizontal distribution trends with a characteristic slight enrichment of MREE in relation to LREE and HREE, as well as with mild negative anomalies of Eu and Ce. Similar distribution trends show that the source of REE in the mineralized dolomite–calcite veins were the host limestones of the Katav formation. At the same time, the contents of Cu and REE have no geochemical connection with each other. In the insoluble mineral residues of the veins, compared with their original composition (see Table 2), the content of Cu increases by 7–10 times, while the amount of REE ($\sim 20\text{--}33\text{ ppm}$) remains at the same level as in the bulk vein samples ($\sim 25\text{ ppm}$). This indicates the absence of a genetic link between REE and ore mineralization, representing an indirect argument in favor of the fact that the source of Cu was not only the host rocks.

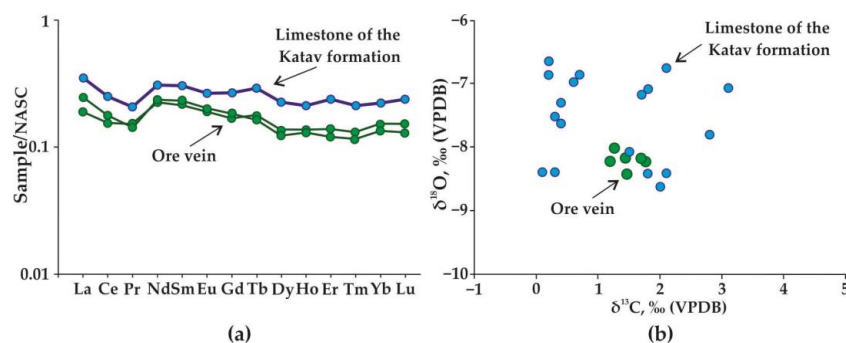


Figure 12. (a) Distribution of REE and (b) isotopic composition of C and O in the dolomite–calcite veins of the Tolparovo ore occurrence and background limestones of the Katav formation outside the ore occurrence. Data on the C and O isotopic composition of Katav formation limestones in the area of Tolparovo village are taken from [91].

5.2.2. C and O Isotopic Composition of Vein Calcite

According to [91], $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the limestones of the Katav formation in the vicinity of Tovparovo village range from 0.1 to 3.1 and from -8.7 to -6.8‰ (VPDB), respectively. According to these studies, the C- and O-isotope signals of the Katav limestones were insignificantly rearranged during the epigenesis, since the geochemical characteristics, typical of unaltered rocks, are preserved in limestones. They demonstrate low Mn/Sr ratios (<3.5) and an absence of correlations between the values of Mn/Sr, Fe/Sr, and $\delta^{18}\text{O}$, on the one hand, and $\delta^{13}\text{C}$, on the other [91]. In terms of C and O isotopic compositions, the dolomite–calcite veins of the Tolparovo ore occurrence are similar to the “background” limestones of the Katav formation (Figure 12b). This indicates that the source of carbon during the formation of the mineralized veins in the ore occurrence was host limestones.

5.2.3. Metal Sources

A comparative analysis of copper background concentrations in the deposits of the Alatau anticlinorium indicates (Figure 13) that, among five formations of the Karatau series, only redbed rocks of the Zilmerdak and Katav formations are enriched in copper. The average Cu content of the Zilmerdak sandstones and Katav limestones (19 ppm, see Table 1) is 1.9–4.7 times higher when compared with the clark of sandstones and carbonate rocks (respectively, $n \times 10^{-4}$ and 4 ppm according to [92]), and 1.2–1.3 times higher compared with the average Cu content of the upper continental crust (14.3 ppm according to [93]). At the same time, the concentrations of copper in the graybed carbonate rocks of the Inzer, Minyar, and Uk formations are at the near-clark level. It follows that a certain copper source in the Tolparovo ore occurrence could be the redbed deposits of the Zilmerdak and Katav formations.

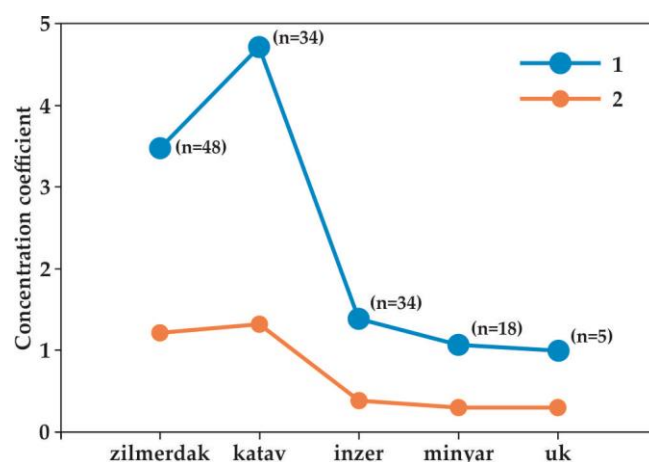


Figure 13. Concentration coefficients of average Cu contents in the rocks of the Karatau series of the Alatau anticlinorium. Legend: 1—relative to the Cu clark of [92]; 2—relative to the average Cu content in the upper continental crust of [93]. *n*—number of samples.

In the fault zone and mineralized veins, contents of TiO_2 , Al_2O_3 , Fe_2O_3 , K_2O , F, V, Cr, Cu, Zn, As, Rb, Ba, and Pb in ore occurrences increase 2–5 times compared with the host rocks (see Table 1). At the same time, the host rocks of the ore occurrence are depleted of the listed elements in comparison with the background limestones of the Katav formation. Consequently, these elements, along with Cu, came from the host rocks to the fault zone. At the same time, among the listed elements, only the Cu and As contents in the fault zone increased significantly, by more than 100 times, compared with the host rocks. This may indicate a partial introduction of Cu and As from an additional source.

In order to determine the source of gold, data on its chemical composition can be used. The ratio of the main components in gold and the content of certain impurity elements may reflect the conditions of its formation and its typomorphic features [64,66,70,94]. Some

phases of Cu-containing gold in the Tolparovo ore occurrence are close to the composition of Cu_3Au_2 . The existence of this gold compound as an independent mineral has not been confirmed so far. In many cases, XRD studies show that Cu_3Au_2 compounds are copper-enriched cuproauride (cubic CuAu) or tetra-auricuprid (tetragonal CuAu) [64,95]. However, Cu-containing gold of such a chemical composition is often found in igneous deposits and the ore occurrences of gold [64,67,68,70]. It should be noted that native gold from the Tolparovo ore occurrence is chemically similar to that of rhodinites in mafite-ultramafite complexes and to gold, associated with gabbrodolerites (see Figure 8b). For example, similar gold compounds have recently been established as a part of a gold–telluride–palladium mineralization in gabbrodolerites of the Pai-Khoi ridge (Russia) [67].

In the Bashkirian uplift, Cu-containing gold of a similar composition was previously found [69] in the endo- and exocontacts of the gabbrodolerite dikes, breaking through the deposits of the neo- and mesoproterozoic in the area of the Aktash ore zone and the Suran sellaite–fluorite deposit. The geological, mineralogical, petrochemical, and geochemical characteristics of gabbrodolerites indicate their belonging to the Inzer gabbrodolerite complex [69]. In both ore zones, gold associates with chalcopyrite and is characterized by a specific composition, where close and significant amounts of Cu (29.8–36.4 wt %) and relatively low Ag contents (4.8–7.8 wt %) are recorded. The constantly present similar and significant Zn impurity (0.8–1.3 wt %) is particularly indicative. Zn represents a rather rare impurity in native gold [64,66,94]. According to the data [94], Zn, along with Pt and Pd, is more common in native gold, associated with relatively low-temperature chloride systems. Geological and geochemical features indicate the genetic relationship of Cu-containing gold in the Western Aktash zone and the Suran deposit with the Inzer gabbrodolerite complex and the activity of postmagmatic fluids [69]. According to [51], the U–Pb age of the Inzer complex is 721 ± 6.9 Ma.

In the Tolparovo ore occurrence, the composition of considered phases is characterized by close quantities of Cu (35.45–40.42 wt %), Ag (4.43–5.08 wt %), and similar contents of Zn (0.64–1.19 wt %) (see Table 7). The ore occurrence is located on the strike line of the Inzer complex gabbrodolerite dikes (see Figure 1b). In our opinion, this fact and similar specific features of the chemical composition for the native gold of the Tolparovo ore occurrence, the Aktash ore zone, and the Suran deposit indicate a single magmatic source of Au in these ore zones.

In the compared ore zones, the common geochemical features of host rocks involve their enrichment in Cu, As, Ba, and Zn. In the Aktash ore zone, at the contact with the dike complex, six copper ore occurrences are localized in Middle Riphean sandstones (see Figure 1a, ore occurrences are indicated by numbers 18–23) with Cu (up to 6.2 wt %), As and Sb (up to 1.0 wt %), Ba (up to 0.5 wt %), Zn (up to 0.3 wt %), and Au (up to 1.0 ppm). An enrichment of ore zones with the same elements, in particular Cu and As, suggests that their additional source in the Tolparovo ore occurrence could be postmagmatic fluids.

It can also be assumed that Ag, Te, and Bi were brought along with Au postmagmatic fluids. This assumption is consistent with the fact that hessite and empressite are not typical minerals in sediment-hosted stratiform copper deposits. Silver tellurides are characteristic of many epithermal gold–telluride deposits [81,96–98] and are often found in deposits of other types (volcanic-hosted massive sulfide (VHMS), intrusion-related gold deposits (IRGD), etc.) e.g., [67,82–84,99,100]. In metamorphogenic–hydrothermal and skarn deposits, gold and silver tellurides, in association with bismuth minerals (wittichenite and Bi-tellurides), are often noted as inclusions in hypogenic bornite [101]. In the ores of almost all sedimentary stratiform copper deposits, silver is a thorough and constantly present element, yet it typically manifests in its native form, its sulfides and sulfosalts, or in amalgams, e.g., [36,49].

Bismuth minerals in the ores of Cu formations similarly belong to relatively rare minerals [10,49]. Wittichenite is most often found among the bismuth minerals of copper deposits, usually intergrowing with bornite and chalcocite and often forming larger nests and flasers in quartz–calcite veins [49]. Bismutite forms in the oxidation zone after wit-

tichenite. Among other bismuth minerals, copper sulfides sometimes associate with native bismuth, bismuthin, which, similar to wittichenite, gravitates towards the bornite zone.

5.3. General Features of Redbed Copper Ore Occurrences of the Bashkirian Uplift

5.3.1. Stratigraphy, Paleogeography, and Paleoclimate

Ore occurrences, localized in the Neoproterozoic deposits on the western slope of the Southern Urals, are characterized by some common features that are typical of stratiform redbed sedimentary–diagenetic copper deposits. First, all known ore occurrences (Lemesa, Zirikly, Katav, Bakeevo, Bolshoy Inzer, Tolparovo, Bolshye Polyany) are stratified. In remote areas of the Bashkirian uplift, they are confined to three close stratigraphic horizons, which form a rather narrow stratigraphic interval in the Neoproterozoic deposits as a whole (see Figure 2). Katav and Lemesa ore occurrences are bedded in sandstones and clay dolostones in the middle part of the Nugush subformation of the Zilmerdak formation [5,6]. The host rocks of Zirikly and Bakeevo ore occurrences are the sandstones of the Bederysh subformation of the Zilmerdak formation. The ore occurrences of Bolshoy Inzer, Tolparovo, and Bolshye Polyany are bedded in red and gray limestones in the lower and middle parts of the Katav formation [1,2]; this article.

Secondly, ore occurrences are found in redbed deposits (see Figure 2, Table 10), where they are typically confined to the boundary of redbed and graybed rocks. At the same time, the highest concentrations of ore elements, for example, in the Bakeevo ore occurrence, are noted mainly in redbed rocks. Bakeevo is the most productive of the considered copper ore occurrences. According to the data of the West Bashkirian complex geological expedition, several ore intervals with a thickness of 1.5–10 m are distinguished herein with a Cu content of 1 wt %.

Table 10. Characteristics of copper ore occurrences in the Neoproterozoic deposits on the western slope of the Southern Urals (compiled according to [1,2,5–7] and the materials of this article).

Occurrence	Stratigraphy	Host Rocks	Mineralization	Inzer Complex Gabbrodolerites
Lemesa	Zl ₂	red and gray dolosiltstones, gray dolostones	Chp, Cc, Bn, Cv	spatial relationship
Katav	Zl ₂	gray sandstones and dolostones	Py, Chp, Sp	not determined
Bakeevo	Zl ₄	red and gray sandstones	no data	established
Zirikly	Zl ₄	red and gray dolosiltstones, gray dolostones	Chp, Cc, Bn, Cv	spatial relationship
Bolshoy Inzer	Kt ₁	red and gray limestones	Py, Chp, Mrc, Gn, Brt	spatial relationship
Tolparovo	Kt ₁	red and gray limestones	Py, Chp, Bn, Dg, Sp, Gn, Ttr-Zn, Wtc, Au, Hes, Eps, Ani, Gee, Cv, Mlc, Azu, Bis, Brt	spatial relationship
Bolshye Polyany	Kt ₁₋₂	gray limestones	Bn, Flr	established

Ani—anilite; Au—native gold; Azu—azurite; Brt—baryte; Bis—bismite; Bn—bornite; Cc—chalcocite; Chp—chalcopyrite; Cv—covellite; Dg—digenite; Eps—empressite; Flr—fluorite; Gee—geerite; Gn—Galena; Hes—hessite; Mlc—malachite; Mrc—marcasite; Py—pyrite; Sp—sphalerite; Ttr-Zn—tetrahedrite-(Zn); Wtc—wittichenite.

Thirdly, a common feature of the host red rocks in the Zilmerdak and Katav formations is the presence of relics of evaporite minerals therein. In redbed sandstones, siltstones and clay shales of the Zilmerdak formation, halite pseudomorphs and numerous shrinkage cracks are found, while, in the redbed clay limestones of the Katav formation, halite and gypsum pseudomorphs are observed [102]. According to the studies [102–104], siliciclastic and carbonate deposits of Zilmerdak and Katav formations were accumulated in arid climates, and in continental and coastal–marine environments, close to evaporite ones.

Most of the world’s stratiform redbed copper deposits are found in sedimentary continental and coastal–marine deposits, accumulated in the arid climates of the low (~20–30°) northern latitudes of the paleoequator [14,105]. The calculated paleo-latitude values for the deposits of the Zilmerdak and Katav formations using the data of [29,30] comprise ~6–18°, respectively, which corresponds to the data reported in [14,105]. The similarity of paleo-

geography determines the proximity of the paleoclimate and sedimentation conditions. With regards to the basal deposits of the Karatau series in the Bashkirian uplift, this similarity allows us to explain the possible cause of increased background Cu concentrations in the rocks of the Zilmerdak and Katav formations (see Figure 13), as well as the confinement of copper ore occurrences to this stratigraphic interval.

In terms of age and sedimentary conditions, the deposits of the Zilmerdak and Katav formations of the Bashkirian uplift are similar to the host rocks of well-known large stratiform deposits of the Central African Copperbelt, which occur in the redbed deposits of the Roan Group with an age of 880–727 Ma [18]. Siliciclastic and carbonate rocks of the Roan group are characterized by the presence of collapse breccias and dissolved relics of evaporite minerals—gypsum and anhydrite pseudomorphs.

According to [8,9,12,14], stratiform copper deposits are associated with intracraton basins, where basal synrift strata of redbed rocks are overlapped by marine and/or lake sediments and by thick evaporite strata in basins located in low latitudes. The presence of redbed rocks and overlapping evaporites form favorable conditions for the formation of the redbed copper deposits [8,9,106,107]. The main source of copper here is redbed hematite-containing layers of rocks with thicknesses typically measured from 100 to 1000 m. According to [8,9], the presence of evaporites leads to the formation of high-saline brines, which can descend into the lower part of sedimentary strata and leach metals from oxidized redbed rocks. During halokinesis, induced by basin inversion, mineralized brines can be discharged in reducing barriers at higher stratigraphic levels [8,9].

At the same time, the studies [106,107] have demonstrated that the amount of pore water, involved in the in situ oxidation of ferrous minerals in redbed formations, is too insignificant for copper transportation. Strictly limited Eh-pH levels of the medium are required for the formation of early-diagenetic copper-containing ore-forming solutions. This researcher believes that these levels can be achieved only in the case of continuous streams of descending oxygen-rich meteoric waters, passing through the evaporite strata. Such solutions can leach copper from the redbed rocks and carry it with the subsequent deposition on reduction barriers.

According to the study of thermodynamic equilibria in redbed copper deposits [19], the process of mineral formation is mainly controlled by the pH of the medium and is weakly dependent on the temperature. At the same time, mineralogical zonality is found in many redbed copper deposits, consisting in the sequential deposition of Fe and Cu sulfides from the edge parts of the ore zones to the central ones in the following order: pyrite → chalcopyrite → bornite → chalcocite [8,14,16,19]. In the Tolparovo ore occurrence, as well as in other ore occurrences of the Bashkirian uplift, the zonal deposition of ore minerals is either absent or rather weakly expressed. According to [7], the copper-sulfide mineral formations in the ore occurrences of Zirikly, Lemesa, and Katav are divided into two types: evaporite and copper sandstones. The evaporite type (Zirikly, Lemesa) is characterized by the azonal scattered distribution of chalcopyrite, bornite, chalcocite, and low Cu content (up to 0.1 wt %) in the host rocks. The type of copper sandstones (Katav) is characterized by the preferential development of chalcopyrite in the rocks, the increased bituminosity of the host rocks, and higher concentrations of Cu (up to 0.6 wt %) [6]. The zonal distribution of copper sulfides and the gradual lateral alteration of the monomineral chalcopyrite mineralization by chalcocite–bornite, then chalcocite, and, finally, sulfide-free zones are assumed only for the type of copper sandstones [7].

5.3.2. Tectonic Control of Mineral Formation and Connection with Intrusive Magmatism

According to the ideas of V.V. Radchenko and G.S. Senchenko [3], copper ore occurrences in the southern part of the Bashkirian uplift (ore occurrences of the Aktash ore zone (see Figure 1a, indicated by numbers 18–23) and some others) represent hydrothermal-metasomatic formations that are localized in the zones of sublatitudinal faults and, especially, at their intersections with submeridional faults. According to these researchers, in these particular zones, the processes of dolomitization and muscovitization are intensively

manifested, acting as indicators of the ore process. This conclusion is confirmed by our studies of the Tolparovo ore occurrence, where ore mineral formation is in paragenetic association with dolomite.

The researchers in [3] believe that the latitudinal faults of the Bashkirian uplift are the deepest and longest-lived. Their formation is associated with the processes of riftogenesis/tafrogenesis, which are accompanied by subalkaline highly titanitic intrusive and effusive volcanism. Indeed, many copper deposits and ore occurrences of the Bashkirian uplift are controlled by sublatitudinal fault zones, traced by gabbrodolerite dikes. For example, Bogryashka copper–gold–sulfide ore occurrence, localized in Lower Riphean deposits (see Figure 1a), is located in the zone of a large sublatitudinal fault [26,58], considered as a reflected foundation fault [50]. Within the area of this occurrence, magmatic formations are represented by a series of heterochronous gabbrodolerite dikes.

The most famous, on the western slope of the Southern Urals' Kiryabinsk and Barsinsk copper–sulfide deposits (see Figure 1a) of a hydrothermal–metasomatic vein type, are confined to a large sublatitudinal tectonic zone [24,108]. The primary ores of these deposits were bedded in the contact zone of the Kiryabinsk peridotite–pyroxenite–gabbro complex with an age of 680 ± 3.4 Ma [109]. This differentiated intrusion is considered a fragment of the concealed Large Igneous Province (LIP) [110].

Eventually, all copper ore occurrences in the Alatau anticlinorium, including the considered Tolparovo occurrence, gravitate to the zones of supposed latitudinal faults. Among these, the Bakeevo ore occurrence is located at the intersection of the latitudinal fault and the Western Kalinsk submeridional thrust (see Figure 1b). At the same time, almost all ore occurrences of copper in the Neoproterozoic deposits of the Bashkirian uplift are associated with dikes of gabbrodolerites of the Inzer complex (see Table 10). They are determined within the area of Bakeevo and Bolshye Polyany ore occurrences [1]. The Bolshoy Inzer and Lemesa ore occurrences are located near the gabbrodolerites of the Inzer complex, while the Tolparovo and Zirikly ore occurrences are on the line of their strike (see Figure 1b). According to our data [69], all copper ore occurrences in the Aktash ore zone are spatially associated with this complex in the southern part of the Bashkirian uplift. These facts allow us to link the copper mineral formation in the ore occurrences of the Alatau anticlinorium with the introduction of the Inzer complex gabbrodolerites and the activity of postmagmatic fluids. The formation time of this complex coincides with the age of Arsha LIP, which was formed at the turn of 707–732 Ma due to the collapse of the Rodinia supercontinent [111,112]. According to V.N. Puchkov [110], Kiryabinsk and Arsha LIPs represent relics of mantle plumes, which, along with a number of other plume events in the Urals, largely determine its metallogeny. At the same time, the main source of copper in the ore occurrences, bedded in the Neoproterozoic deposits of the Bashkirian uplift, apparently, were the host rocks of the Zilmerdak and Katav formations, enriched with Cu at the stage of diagenesis. However, the process of copper leaching from host rocks probably occurred at the stage of epigenesis due to orogenic events and magmatic activity, as demonstrated, for example, for the Central African Copperbelt [43,44]. A similar metallogenic model, linking the copper mineral formation with magmatic activity during the collapse of the Rodinia supercontinent is also proposed for copper deposits in Southern China [45,46].

6. Conclusions

Similar to the world's other stratiform redbed copper deposits, the Bashkirian uplift occurrences are confined to sedimentary deposits that accumulated in an arid climate in near evaporitic continental and coastal–marine settings in the low northern latitudes of the paleoequator. This explains the elevated background concentrations of copper in the host redbed rocks of the Zilmerdak and Katav formations and indicates a predominantly sedimentary source of copper in the Bashkirian uplift.

At the same time, tectonic control is manifested in the location of copper ore occurrences of the Alatau anticlinorium. These deposits are located in the zones of assumed latitudinal faults or at their intersections with the Western Kalinsk submeridional thrust.

Almost all copper ore occurrences in the Neoproterozoic deposits of the Bashkirian uplift are associated with gabbrodolerite dikes of the Inzer complex, which makes it possible to associate the formation of ore occurrences with the activity of postmagmatic fluids. Au, partially Cu and As, and possibly Te, Ag, Bi have a magmatic source. This is indicated by similar features of the chemical composition of native gold from the Tolparovo ore occurrence and other ore zones of the Bashkirian uplift, where it has a similar composition in the gabbroderites of the Inzer complex. The formation time of the Inzer intrusive complex coincides with the age of the Arsha LIP, which represents a relic of the mantle plume and was formed at the turn of 707–732 Ma, in connection with the collapse of the Rodinia supercontinent.

Our study has confirmed the predictions of previous studies concerning the prospects of identifying industrial copper deposits on the western slope of the Southern Urals. The results have both methodological and practical significance in forming the basis for future investigations and prospecting for copper mineralization in Neoproterozoic sediments of the Alatau anticlinorium. The most probable locations of ore accumulations involve fluid discharge zones at the intersections of latitudinal and submeridional faults. Dolomitization and baritization are the indicators of the ore process.

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References

1. Radchenko, V.V. About sulfide mineralization in the southern part of the Bashkir uplift. In *Materials of the Second Scientific Conference of Young Scientists (Geology)*; BBAS USSR: Ufa, Russia, 1971; pp. 81–82.
2. Filippov, V.A.; Akbashev, R.M. To the findings of stratified copper and barite mineralization in the Karatau series of the western slope of the Southern Urals. In *Geology and Conditions of Formation of Copper Deposits in the Southern Urals*; BBAS USSR: Ufa, Russia, 1975; pp. 144–148.
3. Radchenko, V.V.; Senchenko, G.S. Features of tectonics and magmatism of the southern part of the Bashkir uplift in connection with the prospects of ore bearing. In *Geology and Formation of Copper Deposits in the Southern Urals*; BBAS USSR: Ufa, Russia, 1975; pp. 149–152.
4. Alekseev, A.A. Genetic types of copper mineralization and prospects of copper-bearing capacity of the western slope of the Southern Urals. In *Criteria and Methods of Searching for Hidden Pyrite Deposits in the Urals*; BBAS USSR: Ufa, Russia, 1979; pp. 45–47.
5. Filippov, V.A. Prospects for the identification of sedimentary copper deposits in the Upper Riphean deposits of the western slope of the Southern Urals. *Ores Met.* **2009**, *2*, 23–27.
6. Filippov, V.A.; Kutovoy, A.K.; Ryabinin, V.F. A new discovery of copper sulfides in the Zilmerdak formation of the Neoproterozoic on the western slope of the Southern Urals. *Ores Met.* **2015**, *2*, 50–55.
7. Filippov, V.A. Ufa tectonocenter: Features of development in the Neoproterozoic and signs of influence on the migration of hydrocarbons and ore genesis. *Ural. Geol. J.* **2020**, *5*, 35–45. [[CrossRef](#)]
8. Hitzman, M.W.; Kirkham, R.; Broughton, D.; Thorson, J.; Selley, D. The sediment-hosted stratiform copper ore system. In *100th Anniversary Volume*; Society of Economic Geologists: Littleton, CO, USA, 2005; pp. 609–642. [[CrossRef](#)]
9. Hitzman, M.W.; Selley, D.; Bull, S. Formation of sedimentary rock-hosted stratiform copper deposits through Earth history. *Econ. Geol.* **2010**, *105*, 627–639. [[CrossRef](#)]

10. Duczmal-Czernikiewicz, A.; Baibatsha, A.; Bekbotayeva, A.; Omarova, G.; Baisalova, A. Ore minerals and metal distribution in tailings of sediment-hosted stratiform copper deposits from Poland and Kazakhstan. *Minerals* **2021**, *11*, 752. [\[CrossRef\]](#)
11. Aurelien, N.; Ousmane, S.; Pitiya, R.P. Zambia's Copperbelt area and copper mining: A review. *J. Geosci. Environ. Prot.* **2022**, *10*, 67–75. [\[CrossRef\]](#)
12. Kirkham, R.V.; Carriere, J.J.; Laramie, R.M.; Garson, D.F. Global distribution of sediment-hosted stratiform copper deposits and occurrences. *Geol. Surv. Can.* **1995**, *2915*, 256.
13. Gablina, I.F. *Copper Accumulation Conditions in Red Beds Continental Formations*; Nauka: Moscow, Russia, 1983; 112 p.
14. Kirkham, R.V. Distribution, settings, and genesis of sediment-hosted stratiform copper deposits in Boyle sediment-hosted stratiform copper deposits. *Geol. Assoc. Can.* **1989**, *36*, 3–38.
15. Chartrand, F.M.; Brown, A.C.; Kirkham, R.V. Diagenesis, sulphides and metal zoning in the Redstone copper deposit, Northwest Territories. *Geol. Assoc. Can.* **1989**, *36*, 189–206.
16. Cox, D.P.; Lindsey, D.A.; Singer, D.A.; Diggles, M.F. Sediment hosted copper deposits of the world: Deposit model sand database. Open-file report. *US Geol. Surv.* **2003**, *107*, 1–53. [\[CrossRef\]](#)
17. Durieux, C.G.; Brown, A.C. Geological context, mineralization, and timing of the Juramento sediment-hosted stratiform copper-silver deposit. Salta district. Northwestern Argentina. *Miner. Depos.* **2007**, *42*, 879–899. [\[CrossRef\]](#)
18. Zientek, M.L.; Bliss, J.D.; Broughton, D.W.; Christie, M.; Denning, P.D.; Hayes, T.S.; Hitzman, M.W.; Horton, J.D.; Frost-Killian, S.; Jack, D.J.; et al. *Sediment-Hosted Stratabound Copper Assessment of the Neoproterozoic Roan Group, Central African Copperbelt, Katanga Basin, Democratic Republic of the Congo and Zambia*; Scientific Investigations Report 2010–5090–T; US Geological Survey: Reston, VA, USA, 2014; 178p. [\[CrossRef\]](#)
19. Zhang, Y.; Han, R.; Wen, S.; Wei, P. Physiochemical restrictions of mineral zoning of sediment-hosted stratiform copper deposit. *Geofluids* **2018**, *2018*, 4261795. [\[CrossRef\]](#)
20. Khankahdani, K.N.; Karimi, M. Sediment-hosted copper mineralization in Bavanat region. Southern Sanandaj-Sirjan. *J. Sci. Islam. Repub. Iran* **2019**, *30*, 61–75. [\[CrossRef\]](#)
21. Ghasemlou, A.; Kouhestani, H.; Mokhtari, M.A.A.; Zohdi, A. Hamzelou Cu deposit: Redbed type sediment-hosted copper mineralization in the Upper red formation. NW Zanjan. *J. Adv. Appl. Geol.* **2019**, *9*, 480–497. [\[CrossRef\]](#)
22. Sergeeva, N.D. Deposits of the Lower Karatau subseries of the Karatau series of the Alatau anticlinorium in the section along the Zilim river in the area of Tolparovo (Southern Urals). *Geol. Bull.* **2021**, *1*, 3–13. [\[CrossRef\]](#)
23. Larionov, N.N.; Tsvetkova, A.A. *State Geological Map of the Russian Federation, Scale of 1:200,000; Series South Ural. Sheet N-40-XXII (Toucan)*; Ministry of Natural Resources and Environment of the Russian Federation: Saint Petersburg, Russia, 2003.
24. Rykus, M.I.; Snachev, V.I.; Nasibullin, R.A.; Rykus, N.G.; Savelyev, D.E. *Sedimentation, Magmatism and Ore Content of the Northern Part of the Uraltau Zone*; Bashkir State Univ.: Ufa, Russia, 2002; 268p.
25. Dolgov, V.S.; Sereda, M.S.; Kozlov, A.V. *Minerals of the Zlatoust Urals*; FotoMir: Zlatoust, Russia, 2007; 208p.
26. Michurin, S.V.; Kovalev, S.G.; Gorozhanin, V.M. *The Genesis of Sulfates and Sulfides in the Lower Riphean Deposits of the Kamsko-Belsk Avalakogen and Bashkir Meganticlinorium*; Designpoligrafservice: Ufa, Russia, 2009; 192p.
27. Kuznetsov, A.B.; Bekker, A.; Ovchinnikova, G.V.; Gorokhov, I.M.; Vasilyeva, I.M. Unradiogenic strontium and moderate-amplitude carbon isotope variations in early Tonian seawater after the assembly of Rodinia and before the Bitter Springs Excursion. *Precam. Res.* **2017**, *298*, 157–173. [\[CrossRef\]](#)
28. Maslov, A.V.; Erokhin, Y.V.; Gerdes, A.; Ronkin, Y.L.; Ivanov, K.S. First results of U-Pb LA-ICP-MS isotope dating of detrital zircons from arkose sandstone of the Biryán subformation of Zilmerdak formation (Upper Riphean, South Urals). *Dokl. Earth Sc.* **2018**, *482*, 1275–1277. [\[CrossRef\]](#)
29. Golovanova, I.V.; Danukalov, K.N.; Salmanova, R.Y.; Levashova, N.M.; Parfiriev, N.P.; Sergeeva, N.D.; Meert, J.G. Magnetic field hyperactivity during the early Neoproterozoic: A paleomagnetic and cyclostratigraphic study of the Katav formation, southern Urals, Russia. *Geosci. Front.* **2023**, *14*, 101558. [\[CrossRef\]](#)
30. Pavlov, V.; Gallet, Y. Variations in geomagnetic reversal frequency during the Earth's middle age. *Geochem. Geophys. Geosys.* **2010**, *11*, Q01Z10. [\[CrossRef\]](#)
31. Danukalov, K.N.; Golovanova, I.V.; Salmanova, R.Y.; Parfiriev, N.P. Paleomagnetic studies of the Upper Riphean redbeds on the Southern Urals. *Geol. Bull.* **2020**, *3*, 47–54. [\[CrossRef\]](#)
32. Sergeeva, N.D.; Dyakova, S.A. Vend of the eastern flank of the Avdyrdak anticlinal of the Alatau anticlinorium (Southern Urals). *Geol. Bull.* **2023**, *1*, 24–34. [\[CrossRef\]](#)
33. Levashova, N.M.; Bazhenov, M.L.; Meert, J.G.; Kuznetsov, N.B.; Golovanova, I.V.; Danukalov, K.N.; Fedorova, N.M. Paleogeography of Baltica in the Ediacaran: Paleomagnetic and geochronological data from the clastic Zigan Formation, South Urals. *Precam. Res.* **2013**, *236*, 16–30. [\[CrossRef\]](#)
34. Zaitseva, T.S.; Kuznetsov, A.B.; Gorozhanin, V.M.; Gorokhov, I.M.; Ivanovskaya, T.A.; Konstantinova, G.V. The lower boundary of the Vendian in the Southern Urals as evidenced by the Rb–Sr age of glauconites of the Bakeevo formation. *Stratigr. Geol. Correl.* **2019**, *27*, 82–96. [\[CrossRef\]](#)
35. Jowett, E.C. The evolution of ideas about the genesis of stratiform copper-silver deposits. *Econ. Geol.* **1991**, *8*, 117–132.
36. Oummouch, A.; Essaifi, A.; Zayane, R.; Maddi, O.; Zouhair, M.; Maacha, L. Geology and metallogenesis of the sediment-hosted Cu–Ag deposit of Tizert (Igheem inlier. Anti-atlas Copperbelt. Morocco). *Geofluids* **2017**, *2017*, 7508484. [\[CrossRef\]](#)

37. Hitzman, M.W.; Broughton, D.W. Discussion: «Age of the Zambian Copperbelt» by Sillitoe et al. *Miner. Depos.* **2017**, *52*, 1273–1275. [\[CrossRef\]](#)
38. Sillitoe, R.H.; Perello, J.; Creaser, R.A.; Wilton, J.; Wilson, A.J.; Dawborn, T. Reply to discussions of «Age of the Zambian Copperbelt» by Hitzman and Broughton and Muchez et al. *Miner. Depos.* **2017**, *52*, 1277–1281. [\[CrossRef\]](#)
39. Shubin, Y.P. Features of the material composition, genesis and control of copper mineralization of the Bakhmut basin of Donbass. *Collect. Sci. Pap. SEI HE «DonSTI» (LPR)* **2020**, *20*, 23–30.
40. Chen, G.; Chen, M.; Ke, C.; Tang, Y. Paleozoic VMS-type stratiform mineralization overprinted by Mesozoic vein-type mineralization in the Yushui copper deposit. Eastern Guangdong. South China. *Ore Geol. Rev.* **2023**, *158*, 105498. [\[CrossRef\]](#)
41. Barra, F.; Broughton, D.; Ruiz, J.; Hitzman, M. Multi-stage mineralization in the Zambian Copperbelt based on Re-Os constraints. *Geol. Soc. Am. Abstr. Programs* **2004**, *36*, 516.
42. Muchez, P.; Andre-Mayer, A.S.; Desouky, H.A.E.; Reisberg, L. Diagenetic origin of the stratiform Cu-Co deposit at Kamoto in the Central African Copperbelt. *Miner. Depos.* **2015**, *50*, 437–447. [\[CrossRef\]](#)
43. Sillitoe, R.H.; Perello, J.; Creaser, R.A.; Wilton, J.; Wilson, A.J.; Dawborn, T. Age of the Zambian Copperbelt. *Miner. Depos.* **2017**, *52*, 1245–1268. [\[CrossRef\]](#)
44. Saintilan, N.J.; Selby, D.; Creaser, R.A.; Dewaele, S. Sulphide Re-Os geochronology links orogenesis, salt and Cu-Co ores in the Central African Copperbelt. *Sci. Rep.* **2018**, *8*, 14946. [\[CrossRef\]](#)
45. Qiu, H.N.; Zhu, B.Q.; Sun, D.Z. Age significance interpreted from $^{40}\text{Ar}/^{39}\text{Ar}$ dating of quartz samples from the Dongchuan Copper Deposits (Yunnan, SW China) by crushing and heating. *Geochem. J.* **2002**, *36*, 475–491. [\[CrossRef\]](#)
46. Ye, L.; Liu, Y.P.; Li, C.Y.; Liu, J.J. The Ar-Ar isotopic age in Dongchuan Taoyuan type copper deposit. Yunnan Province and its significance. *Miner. Petrol.* **2004**, *24*, 57–60.
47. Zhao, X.F.; Zhou, M.F.; Li, J.W.; Qi, L. Late Paleoproterozoic sedimentary rock-hosted stratiform copper deposits in South China: Their possible link to the supercontinent cycle. *Miner. Depos.* **2013**, *48*, 129–136. [\[CrossRef\]](#)
48. Cailteux, J.L.H.; Kampunzu, A.B.; Lerouge, C.; Kaputo, A.K.; Milesi, J.P. Genesis of sediment-hosted stratiform copper–cobalt deposits, central African Copperbelt. *J. Afr. Earth Sci.* **2005**, *42*, 134–158. [\[CrossRef\]](#)
49. Trubachev, A.I.; Korolkov, A.T.; Radomskaya, T.A. Parageneses of minerals and forms of their recognition reflecting the stages of formation of cupriferous sandstones and shales deposit. *Bull. Tomsk Polytech. Univ. Geo Assets Eng.* **2019**, *330*, 70–89. [\[CrossRef\]](#)
50. Larionov, N.N.; Bergazov, I.R.; Granovskaya, N.V.; Nigmatullina, A.M. *State Geological Map of the Russian Federation, Scale of 1:200,000*, 2nd. ed.; Series South Ural. Sheet N-40-XXII (Toucan). Explanatory not; The Moscow branch–A.P. Karpinsky Russian Geological Research Institute: Moscow, Russia, 2015.
51. Knyazev, Y.G.; Knyazeva, Y.G.; Snachev, V.I.; Karimov, T.R.; Masagutov, R.K.H.; Bykova, L.S.; Utaev, M.A.; Aidarov, E.M.; Alslanova, E.R. *Report on the Results of Work on the Object: “Creation of a set of the State Geological Map, Scale of 1:1,000,000. Sheet N-40-Ufa”*; A.P. Karpinsky Russian Geological Research Institute: St. Petersburg, Russia, 2013; 512p.
52. Kozlov, V.I. *The Upper Riphean and the Vend of the Southern Urals*; Nauka: Moscow, Russia, 1982; 128p.
53. Karamova, A.M.; Kazbulatova, G.M.; Michurin, S.V.; Zakharova, A.G. Photometric method of determination of fluorine in rocks by formation of alizarin complexone–lanthanide(III)–fluoride. *Bashkir Chem. J.* **2019**, *26*, 42–47.
54. Gromet, L.P.; Dymek, R.F.; Haskin, L.A.; Korotev, R.L. The «North American shale composite»: Its compilation, major and trace element characteristics. *Geochim. Cosmochim. Acta* **1984**, *48*, 2469–2482. [\[CrossRef\]](#)
55. Cathelineau, M. Cation site occupancy in chlorites and illites as a function of temperature. *Clay Miner.* **1988**, *23*, 471–485. [\[CrossRef\]](#)
56. Hey, M.H. A new review of chlorites. *Miner. Mag.* **1954**, *30*, 277–292. [\[CrossRef\]](#)
57. Talantsev, A.S. *Geothermobarometer by Dolomite–Calcite Paragenesis*; Nauka: Moscow, Russia, 1981; 136p.
58. Sharipova, A.A. Mineralogy and Geochemistry of Gold Deposits and Ore Occurrences of the Avzyan Ore Region (Southern Urals). Ph.D. Thesis, Kazan Federal University, Kazan, Russia, 2021.
59. Chang, Y.A.; Goldberg, D.; Neumann, J.P. Phase diagrams and thermodynamic properties of ternary gold–copper–silver systems. *J. Phys. Chem. Ref. Data* **1977**, *6*, 621–674. [\[CrossRef\]](#)
60. Murzin, V.V.; Malyugin, A.A. New data on the instability of natural solid solutions of the Au–Ag–Cu system in the temperature range below 350 °C. *Rep. USSR Acad. Sci.* **1983**, *269*, 723–724.
61. Knight, J.; Leitch, C.H.B. Phase relations in the system Au–Cu–Ag at low temperatures based on natural assemblages. *Can. Mineral. J.* **2001**, *39*, 889–905. [\[CrossRef\]](#)
62. Chudnenko, K.V.; Palyanova, G.A. Thermodynamic modeling of native formation Cu–Ag–Au–Hg solid solutions. *Appl. Geochem.* **2016**, *66*, 88–100. [\[CrossRef\]](#)
63. Prince, A.; Velikanova, T.; Turchanin, M.A. *Silver–Gold–Copper. Ternary Alloy Systems. Phase Diagrams, Crystallographic and Thermodynamic Data. Landolt Boernstein, Numerical Data and Functional Relationships in Science and Technology (New Series); Group IV: Physical Chemistry*; Martiensen, W., Effenberg, G., Ilyenko, S., Eds.; Library of Congress Cataloging: Germany, Berlin, 2006; pp. 10–41.
64. Spiridonov, E.M.; Pletnev, P.A. *The Deposit of Copper Gold Zolotaya Gora (about the «Gold-Rodingite» Formation)*; Nauchny Mir: Moscow, Russia, 2002; 216p.
65. Moles, N.; Chapman, R.J.; Warner, R. The significance of copper concentrations in natural gold alloy for reconnaissance exploration and understanding gold-depositing hydrothermal systems. *Geochem Explor. Environ. Anal.* **2013**, *13*, 115–130. [\[CrossRef\]](#)

66. Palyanova, G.A. Gold and silver minerals in sulfide ore. *Geol. Ore Dep.* **2020**, *62*, 383–406. [\[CrossRef\]](#)
67. Shaybekov, R.I.; Sokerina, N.V.; Isaenko, S.I.; Zysin, N.N.; Shanina, S.N. Gold–telluride–palladium mineralization, a new type of mineralization in gabbro-dolerites of the Pai-Khoi Ridge (Yugor Peninsula, Russia). *Russ. Geol. Geophys.* **2020**, *61*, 268–285. [\[CrossRef\]](#)
68. Yurichev, A.N. Gold and silver accessory minerals in ultramafites of the Kyzыр-Burlyuksky ultramafic massif (Western Sayan). *Ores Met.* **2021**, *4*, 109–120. [\[CrossRef\]](#)
69. Michurin, S.V.; Sharipova, A.A. The first finds of copper gold in the Riphean deposits of the Bashkir meganticlinorium (Southern Urals). *Bull. Voronezh State Tech. University. Ser. Geol.* **2022**, *3*, 52–65.
70. Murzin, V.; Palyanova, G.; Mayorova, T.; Beliaeva, T. The gold–palladium Ozernoe occurrence (Polar Urals, Russia): Mineralogy, conditions of formation, sources of ore matter and fluid. *Minerals* **2022**, *12*, 765. [\[CrossRef\]](#)
71. Tauson, V.L.; Makeyev, A.V.; Akimov, V.V.; Paradina, L.F. Copper distribution in minerals of zinc sulfide. *Geochemistry* **1988**, *4*, 492–505.
72. Hardardottir, V.; Hannington, M.; Hedenquist, J.; Kjarsgaard, I.; Hoal, K. Cu-rich scales in the reykjanes geothermal system, Iceland. *Econ. Geol.* **2010**, *105*, 1143–1155. [\[CrossRef\]](#)
73. Raabe, K.C.; Sack, R.O. Growth zoning in tetrahedrite-tennantite from the Hock Hocking mine, Alma, Colorado. *Can. Miner.* **1984**, *22*, 577–582.
74. Lyubimtseva, N.G.; Prokofieva, V.; Bortnikov, N.S. Coexisting tetrahedrite–(Zn) and sphalerite at the Teremki Gold-Ore Deposit (East Transbaikalia): Chemical composition and formation conditions. *Geol. Ore Dep.* **2021**, *63*, 454–464. [\[CrossRef\]](#)
75. Lusk, J.; Calder, B.O.E. The composition of sphalerite and associated sulfides in reactions of the Cu–Fe–Zn–S, Fe–Zn–S and Cu–Fe–S systems at 1 bar and temperatures between 250 and 535 °C. *Chem. Geol.* **2004**, *203*, 319–345. [\[CrossRef\]](#)
76. Kojima, S.; Sugaki, A. Phase relations in the Cu–Fe–Zn–S system between 500 and 300 °C under hydrothermal conditions. *Econ. Geol.* **1985**, *80*, 158–171. [\[CrossRef\]](#)
77. Barton, P.B., Jr.; Skinner, B.J. Sulfide mineral stabilities. In *Geochemistry of Hydrothermal Ore Deposits*, 2nd ed.; Barnes, H.L., Ed.; Wiley: New York, NY, USA, 1979; pp. 278–403.
78. Afifi, A.M.; Kelly, W.C.; Essene, E.J. Phase relations among tellurides, sulfides, and oxides; Pt. II. Applications to telluride-bearing ore deposits. *Econ. Geol.* **1988**, *83*, 395–404. [\[CrossRef\]](#)
79. Karakaya, I.; Thompson, W.T. The Ag–Te (silver–tellurium) system. *J. Phase Equilibria* **1991**, *12*, 56–63. [\[CrossRef\]](#)
80. Voronin, M.V.; Osadchii, E.G.; Brichkina, E.A. Thermochemical properties of silver tellurides including empressite (AgTe) and phase diagrams for Ag–Te and Ag–Te–O. *Phys. Chem. Miner.* **2017**, *44*, 639–653. [\[CrossRef\]](#)
81. Zhai, D.; Liu, J. Gold–telluride–sulfide association in the Sandaowanzi epithermal Au–Ag–Te deposit, NE China: Implications for phase equilibrium and physicochemical conditions. *Miner. Petrol.* **2014**, *108*, 853–871. [\[CrossRef\]](#)
82. Liu, J.; Wang, Y.; Huang, S.; Wei, R.; Sun, Z.; Hu, Q.; Hao, J. The gold occurrence in pyrite and Te–Bi mineralogy of the Fancha gold deposit, Xiaoqinling gold field, southern margin of the North China Craton: Implication for ore genesis. *Geol. J.* **2019**, *55*, 5791–5811. [\[CrossRef\]](#)
83. Alfonso, P.; Ccolque, E.; Garcia-Valles, M.; Martinez, A.; Yubero, M.T.; Anticoi, H.; Sidki-Rius, N. Mineralogy and mineral chemistry of the Au–Ag–Te–(Bi–Se) San Luis Alta Deposit, Mid-South Peru. *Minerals* **2023**, *13*, 568. [\[CrossRef\]](#)
84. Vikentyev, I.V. Precious metal and telluride mineralogy of large volcanic-hosted massive sulfide deposits in the Urals. *Miner. Petrol.* **2006**, *87*, 305–326. [\[CrossRef\]](#)
85. Fleet, M.E. Phase equilibria at high temperatures. *Rev. Miner. Geochem.* **2006**, *61*, 365–419. [\[CrossRef\]](#)
86. Craig, J.R.; Scott, S.D. Sulfide phase equilibria: Reviews in Mineralogy. *Miner. Soc. Am.* **1976**, *1*, CS1–CS110.
87. Whiteside, L.S.; Goble, R.Y. Structural and compositional changes in copper sulfides during leaching and dissolution. *Can. Miner.* **1986**, *24*, 247–258.
88. Brugger, J.; Ogierman, J.; Pring, A.; Waldron, H.; Kolitsch, U. Origin of the secondary REE-minerals at the Paratoo copper deposit near Yunta. *S. Aus. Mag. Miner.* **2006**, *70*, 609–627. [\[CrossRef\]](#)
89. Sawlowicz, Z. REE and their relevance to the development of the Kupferschiefer copper deposit in Poland. *Ore Geol. Rev.* **2013**, *55*, 176–186. [\[CrossRef\]](#)
90. Sadati, S.N.; Mao, J.; Yazdi, M.; Benzadi, M.; Adabi, M.H.; Xu, L.; Mokhtari, M.A.A. REE distribution during diagenetic processes of sedimentary copper deposit in Nahand-Ivand Area. NW Iran. *Acta Geol. Sin. Engl.* **2014**, *88*, 460–462. [\[CrossRef\]](#)
91. Kuznetsov, A.B.; Semikhatov, M.A.; Maslov, A.V.; Gorokhov, I.M.; Prasolov, E.M.; Krupenin, M.T.; Kislova, I.V. New data on Sr-and C-isotopic chemostratigraphy of the Upper Riphean type section (Southern Urals). *Stratigr. Geol. Correl.* **2006**, *14*, 25–53. [\[CrossRef\]](#)
92. Turekian, K.K.; Wedepohl, K.H. Distribution of the elements in some major units of the earth's crust. *Geol. Soc. Am. Bull.* **1961**, *72*, 175–192. [\[CrossRef\]](#)
93. Wedepohl, K.H. The composition of the continental crust. *Geochim. Cosmochim. Acta* **1995**, *59*, 1217–1232. [\[CrossRef\]](#)
94. Chapman, R.J.; Banks, D.A.; Styles, M.T.; Walshaw, R.D.; Piazzolo, S.; Morgan, D.J.; Grimshaw, M.R.; Spence-Jones, C.P.; Matthews, T.J.; Borovinskaya, O. Chemical and physical heterogeneity within native gold: Implications for the design of gold particle studies. *Miner. Depos.* **2021**, *56*, 1563–1588. [\[CrossRef\]](#)

95. Zaccarini, F.; Pushkarev, E.; Garuti, G.; Krause, J.; Dvornik, G.P.; Stanley, C.; Bindi, L. Platinum-group minerals (PGM) nuggets from alluvial-eluvial placer deposits in the concentrically zoned mafic-ultramafic Uktus complex (Central Urals, Russia). *Eur. J. Miner.* **2013**, *25*, 519–531. [\[CrossRef\]](#)
96. Pals, D.W.; Spry, P.G. Telluride mineralogy of the low-sulfidation epithermal Emperor gold deposit, Vatukoula, Fiji. *Miner. Petrol.* **2003**, *79*, 285–307. [\[CrossRef\]](#)
97. Spry, P.G.; Scherbath, N.L. The gold-vanadium-tellurium association at the Tuvatu gold-silver prospect, Fiji: Conditions of ore deposition. *Miner. Petrol.* **2006**, *87*, 171–176. [\[CrossRef\]](#)
98. Bortnikov, N.S.; Volkov, A.V.; Savva, N.E.; Prokofiev, V.Y.; Kolova, E.E.; Dolomanova-Topol, A.A.; Galyamov, A.L.; Murashov, K.Y. Epithermal Au–Ag–Se–Te deposits of the Chukchi Peninsula (Arctic zone of Russia): Metallogeny, mineral assemblages and fluid regime. *Russ. Geol. Geophys.* **2022**, *63*, 435–457. [\[CrossRef\]](#)
99. Maslennikov, V.V.; Ayupova, N.R.; Safina, N.P.; Tseluyko, A.S.; Melekestseva, I.Y.; Large, R.R.; Herrington, R.J.; Kotlyarov, V.A.; Blinov, I.A.; Maslennikova, S.P.; et al. Mineralogical features of ore diagenites in the Urals massive sulfide deposits, Russia. *Minerals* **2019**, *9*, 150. [\[CrossRef\]](#)
100. Novakov, R.M.; Kungurova, V.E.; Moskaleva, S.V. Formation conditions of noble metal mineralization in sulfide cobalt-copper-nickel ores of Kamchatka (on the example of Annabergitovaya Schel ore occurrence). *J. Min. Inst.* **2021**, *248*, 209–222. [\[CrossRef\]](#)
101. Cook, N.J.; Ciobanu, C.L.; Danyushevsky, L.V.; Gilbert, S. Minor and trace elements in bornite and associated Cu–(Fe)-sulfides: A LA-ICP-MS study. *Geochim. Cosmochim. Acta* **2011**, *75*, 6473–6496. [\[CrossRef\]](#)
102. Maslov, A.V.; Krupenin, M.T.; Gareev, E.Z. Lithological, lithochemical and geochemical indicators of paleoclimate: Evidence from Riphean of the Southern Urals. *Lith. Miner. Res.* **2003**, *38*, 427–446. [\[CrossRef\]](#)
103. Parnachev, V.P. Fluorine and chlorine in Late Precambrian sedimentary rocks of the Bashkir uplift in connection with the issues of their sedimentogenesis. In *Geochemistry of Volcanic and Sedimentary Rocks of the Southern Urals*; UB RAS: Sverdlovsk, Russia, 1987; pp. 35–47.
104. Gareev, E.Z. Geochemistry of Sedimentary Rocks of the Stratotypic Riphean Section, Academic Degree of Candidate of Geological and Mineralogical Sciences. Ph.D. Thesis, V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow, Russia, 1989.
105. Strakhov, N.M. Principles of lithogenesis. *Geol. Mag.* **1962**, *3*, 577. [\[CrossRef\]](#)
106. Brown, A.C. A process-based approach to estimating the copper derived from redbeds in the sediment-hosted stratiform copper model. *Econ. Geol.* **2009**, *104*, 857–868. [\[CrossRef\]](#)
107. Brown, A.C. Constraints on conceptual and quantitative modeling of early diagenetic sediment-hosted stratiform copper mineralization. *Minerals* **2017**, *7*, 192. [\[CrossRef\]](#)
108. Kovalev, S.G.; Salikhov, D.N.; Puchkov, V.N. *Mineral Resources of the Republic of Bashkortostan (Metals)*; Alfa-Reklama: Ufa, Russia, 2016; 554p.
109. Krasnobaev, A.A.; Puchkov, V.N.; Sergeeva, N.D.; Lepekhina, E.N. Zirconology of pyroxenites from the Kiryabinka pyroxenite-gabbro complex (Southern Urals). *Dokl. Earth Sc.* **2013**, *450*, 531–535. [\[CrossRef\]](#)
110. Puchkov, V.N. General features relating to the occurrence of mineral deposits in the Urals: What, where, when and why. *Ore Geol. Rev.* **2016**, *85*, 4–29. [\[CrossRef\]](#)
111. Puchkov, V.N. The Plumes—A new word in geology of the Urals. *Litosfera* **2018**, *18*, 483–499. [\[CrossRef\]](#)
112. Puchkov, V.N.; Ernst, R.E.; Ivanov, K.S. The importance and difficulties of identifying mantle plumes in orogenic belts: An example based on the fragmented large igneous province (LIP) record in the Ural fold belt. *Precam. Res.* **2021**, *361*, 106–186. [\[CrossRef\]](#)

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