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Article

Mineral and S-Isotope Compositions of Cu-Sulfide Deposits in Southern Siberia (Kodar–Udokan Region), Russia

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Abstract: The Kodaro–Udokan region is a huge Cu metallogenic province in Southern Siberia, one of the largest on Earth. It contains world-class copper sandstone-hosted Udokan (Cu reserves of 26.7 Mt) and PGE-Ni-Cu Chineysky deposits related to gabbro–anorthosite pluton (Cu—10 Mt; Fe-Ti-V, 30 Gt of ore). Furthermore, there are many small deposits of sulfide ores in sedimentary and igneous rocks in this region as well. For many decades, their genesis has been hotly debated. We studied the mineral composition and the sulfur isotopes in several deposits located at different levels of the stratigraphic sequence and in gabbro intruded in sandstones of the Udokan complex. The differences in ore compositions were found. The Burpala and Skvoznoy deposits consisting of the chalcocite–bornite association are characterized only by negative $\delta^{34}S$. The $\delta^{34}S$ values for the Udokan deposits are mostly <0 (up to −28‰). The positive $\delta^{34}S$ data characterize the ores of the Chineysky and Luktursky intrusions. Two Cu sandstone-hosted deposits are characterized by complex ore composition, i.e., the Krasny deposit, comprising chalcopyrite–pyrrhotite ores, is enriched in Co, Ni, Bi, Sb, Mo, Pb, Zn, Se, Te, and U and has a wide range of $\delta^{34}S$ = −8.1–+13.5‰, and the Pravoingamakitsky deposit (Basaltovy section), consisting of quartz–chalcopyrite veins, has high PGE contents in ores with $\delta^{34}S$ = +2.9–+4.0‰. These deposits are located near the gabbro massifs, and it is supposed that their ore compositions were influenced by magmatic fluids. The general regularities of the localization of the deposits in rift zones, and the proximity of mineral and isotopic composition allow us to conclude that the main source of copper could be rocks of basic composition because only they contain high Cu contents. Fluids from deep zones could penetrate to the surface and form Cu sandstone-hosted deposits.

Keywords: Cu sandstones; gabbro–anorthosite; Chineysky pluton; S isotopes; chalcopyrite; bornite; chalcocite; magmatic ore

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1. Introduction

Southern Siberia represents a huge Paleoproterozoic metallogenic province, one of the largest not only in Russia but also in the world [1–5]. It includes substantial copper deposits with varying amounts of silver, iron, vanadium, and other metals. Deposits localized in sandstones and gabbro–anorthosite layered Chineysky pluton in the Kodar–Udokan region contain more than 50 million tons of copper: 26.7 Mt from the Udokan deposit, 12 Mt from its satellite deposit [6], and around 15 Mt from the Chineysky deposits [7]. All of them are concentrated in a small territory (50 km × 50 km) and are characterized by different ore compositions. The dominance of copper in them raises the question of their genetic relationships, which goes beyond the geology of ore deposits and includes the problems of magmatism, tectonics, sedimentology, and geochemistry.

First of all, this province contains the world-class Udokan deposit of cuprous sandstones enriched in Fe, Ag, and Au [6]. It is accompanied by similar deposits ranging from small to large with associated elements (Ag, Se, and Te). The second very important type of deposit includes Cu magmatic ores in layered intrusions in combination with V-rich titanomagnetite ores. The giant Chineysky deposits of this type are related to the gabbro–anorthosite pluton of the same name [8–10]. There are some smaller deposits around it. The third, the rarest type of deposit, is represented by hydrothermal veins with copper mineralization in the vicinity of the Chineysky pluton (80 m from its contact).

The copper enrichment of this large block of the Earth's crust in the south of the Siberian Platform raises the question of a possible genetic link between the deposits of this area. It includes the question of copper sources, the mechanisms of its concentration, and the inheritance of the ore formation processes. Even though increased concentrations of copper in sedimentary rocks are established on the periphery of practically all large cratons [11], including the Siberian craton (Figure 1), and are also observed in ultramafic–mafic intrusions, large deposits are absent in most places. Therefore, the determination of the conditions of the formation of the deposits localized in the Kodar–Udokan area represents a fundamental geological problem, which also has an important applied significance: the peculiarities of ore formation should be used in the prospecting of new deposits.

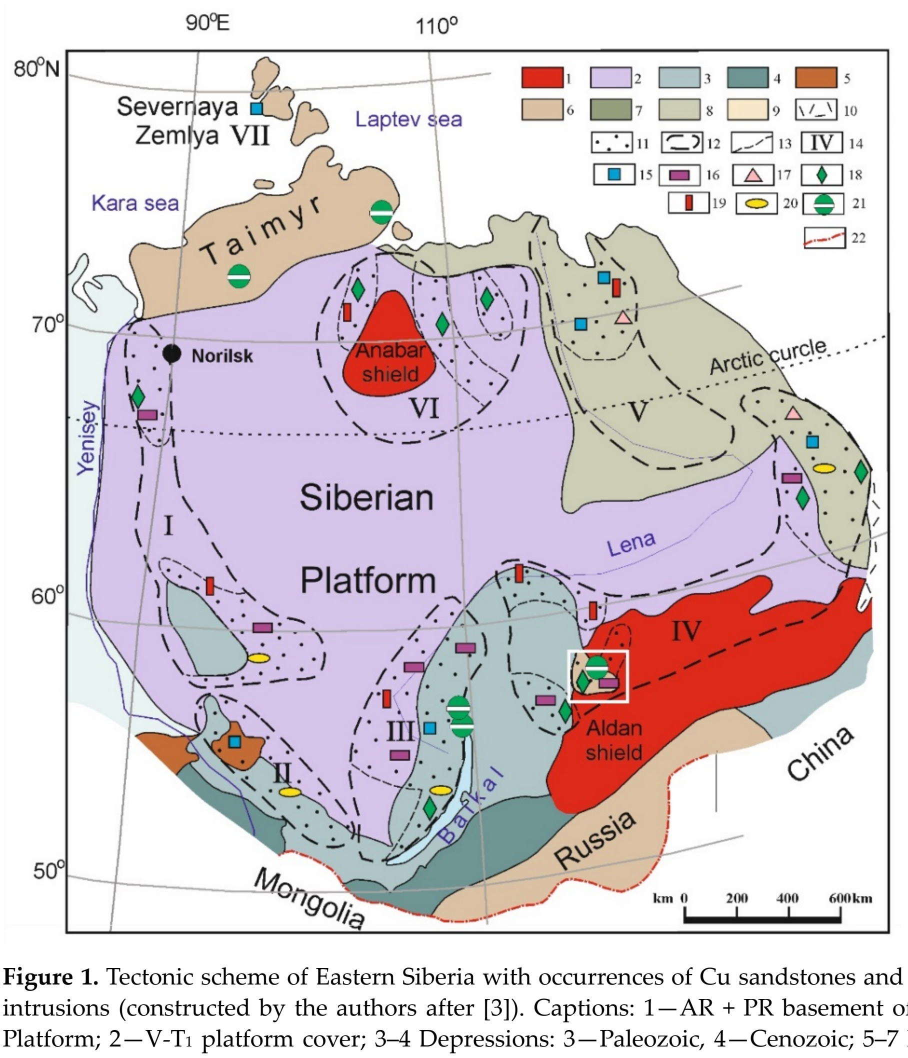


Figure 1. Tectonic scheme of Eastern Siberia with occurrences of Cu sandstones and large layered intrusions (constructed by the authors after [3]). Captions: 1—AR + PR basement of the Siberian Platform; 2—V-T_1 platform cover; 3–4 Depressions: 3—Paleozoic, 4—Cenozoic; 5–7 Folded areas: 5—Riphean–Vendian, 6—Silurian–Devonian, 7—Carboniferous–Permian; 8—Proterozoic deposits; 9—Mesozoic deposits; 10—Volcanic troughs; 11—Cu sandstone areas; 12–13 Boundaries: 12—Copper provinces, 13—Areas of Cu sandstones; 14—Number of the provinces; 15–20 Copper deposits and occurrences: 15—Proterozoic, 16—Vendian, 17—Cambrian, 18—Ordovician, 19—Devonian, 20—Carboniferous; 21—Large layered intrusions; 22—Boundary of Russia. White square is Kodar–Udokan region. I–VII Cu metallogenic provinces: I—Igarka–Yenisey, II—Sayan, III—Baikal, IV—Aldan, V—Verkhoyansk, VI—Anabar, VII—Severnaya Zemlya.

The main problems of the genesis of deposits of the Kodaro–Udokan region, especially those localized in sedimentary rocks, have been discussed for several decades since the discovery of the Udokan deposit in 1949. The most widespread hypothesis of this unique deposit is the assumption of its purely sedimentary genesis [12–19], i.e., ore formation due to transported sulfides from destroyed ancient copper deposits redeposited by channel flows. However, neither the root source of such deposits was found nor the possibility of transporting brittle sulfides over long distances (hundreds to thousands of kilometers) was demonstrated. Moreover, sulfides rapidly oxidized in the post-GOE (Great Oxidation Event) atmosphere. Sochava [20] put forward a more realistic hydrothermal-sedimentary idea of ore formation, suggesting the leading role of sulfate-reducing bacteria. However, the sources of copper and sulfur have remained unclear until now.

The formation of ores in gabbro is almost unambiguously recognized as magmatic, but the essentially copper composition of the ores compared to other typical copper–nickel deposits of this type require explanation. Attempts to resolve the questions about the origin of the two types of ores were reduced to possible genetic links between the deposits formed by them: either the basic magmas that formed the massifs of the Chineysky complex assimilated copper-bearing sandstones of the Udokan complex [16,21], or hydrothermal fluids separated during crystallization of basic magmas were the source of the ore for the hydrothermal deposits in sandstone (such as the Pravoingamakitsky deposit [22]). Despite the fact that the Chineysky massif intrudes the rocks of the Udokan series and is younger compared to them (1.86 Ga [23] related to 1.89 [24] for Udokan), the question of the relationship between the sedimentary and the igneous ores is not resolved because the age of the mineralization itself in the sandstone was not determined. The age of the Udokan series reflects only the age of the sediments, not the mineralization, which can be younger than the host rocks. Therefore, there is a theoretical possibility of mineralization formation after the host rocks and its genetic connection with the huge volume of basic magmas in the Kodaro–Udokan trough. In this case, magmatic rocks and related fluids could have an important role in the origin of ores in sandstones.

As a rule, these ideas remain at the level of assumptions. One of the approaches to the solution of the question about the genesis of ores is the study of the sulfur isotope composition in the sulfides of ore deposits and the oxygen isotopes in rocks. Previously obtained data were extremely limited [25,26] and did not allow for solving the problem. The expansion of these works, including the study of objects of "intermediate" type between the two main types of deposits, allows us to approach the problem of the genesis of deposits in the Kodar–Udokan area in a more reasoned manner, indicating more complex relationships between the ores and their complex character, which is shown below.

2. Geological Background

2.1. Brief Geology of the Territories

The Kodar–Udokan complex is subdivided into three series (Kodarsky, Chineysky, and Kemensky) and nine formations forming gentle folds [27,28]. It is assumed that the sedimentation process for the two latest series took place in the interval of 1.90–1.87 Ga, no more than 30 Ma [29,30]. The deposits are situated at different levels of the sedimentary sequence. The Kodarsky series comprises numerous pyrrhotite horizons with pyrite and chalcopyrite, enriched in Ag, Co, and Ni. The middle, the Chineysky series (Chitkandinsky and Alexandrovsky formations), contains Pravoingamakitsky, Krasny, and other deposits and ore occurrences. The upper, the Kemensky series, is characterized by the maximum mineralization within the Sakukansky Formation, where the main ore horizon of the Udokan deposit occurs. These rocks were formed 1896 ± 2 Ma ago according to ID TIMS U-Pb data on titanite from the ore zone [24]. The Talakansky Formation localizes the Unkur and Burpala deposits.

The rocks of the Udokan complex are intruded by alkaline granites of the Katuginsky and granites of the Kodarsky complexes, as well as basic–ultrabasic rocks of the

Chineysky complex. The latter combines several massifs and dykes mostly consisting of gabbro. The largest intrusion is the Chineysky layered pluton at about 3 km thick [8,9]. It consists of gabbro, titanomagnetite gabbro, anorthosite, and, rarely, norites. Titanomagnetite ores form a unique vanadium deposit, the largest in Russia. Sulfide mineralization occurs within the contact zone of the intrusion with the sandstones of the Udokan complex forming a large Cu deposit. Similar mineralization is related to the Luktursky and Mylovsky massifs [9] (Figure 2).

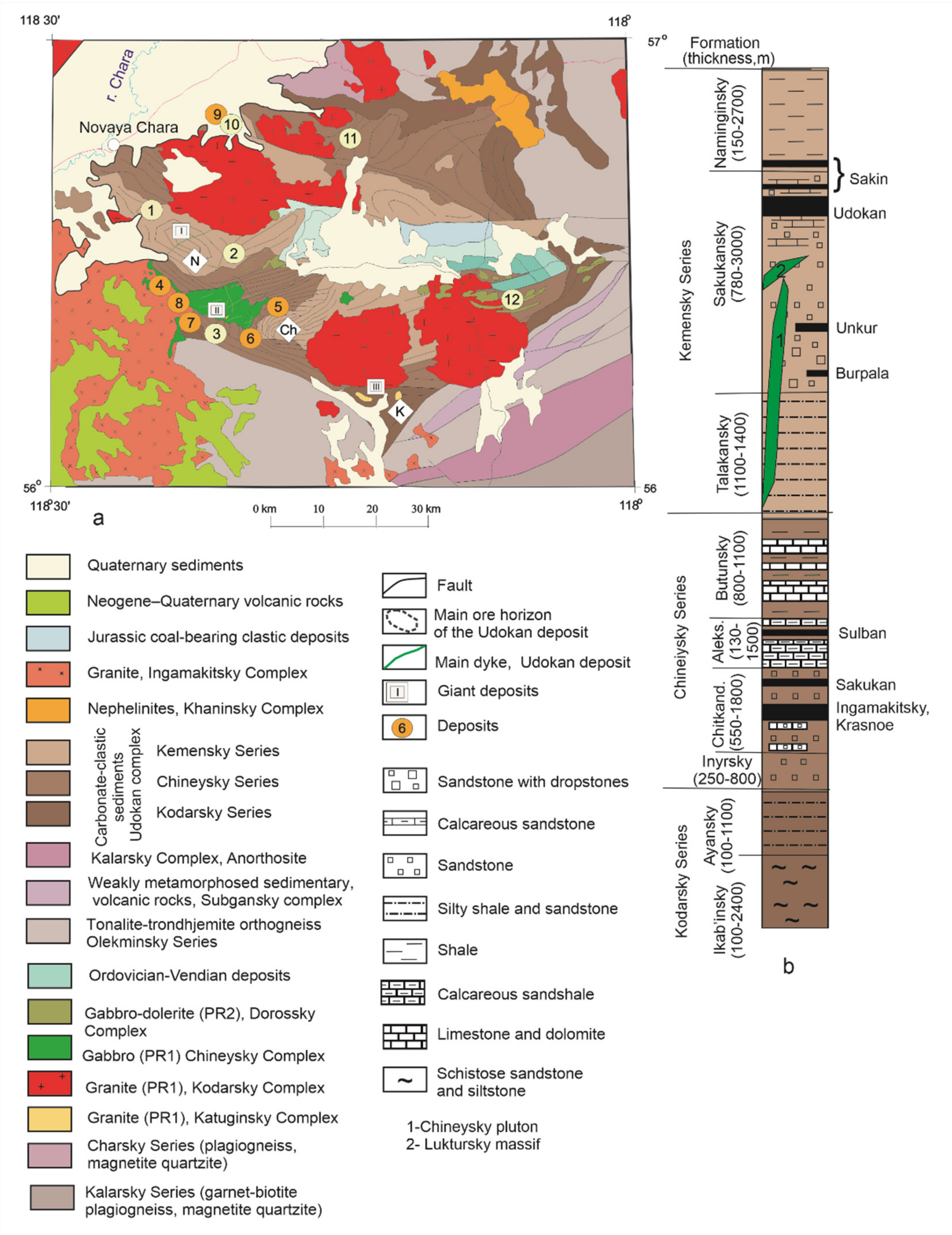


Figure 2. Geological map (**a**) and stratigraphic column (**b**) with the setting of Cu deposits in the Kodar–Udokan region (modified by the authors after Chitageologia data). Abbreviations, formations: Aleks.—Aleksandrovsky; Chitkand.—Chitkandinsky; Superlarge ore deposits: I—Udokan, II—Chineysky, III—Katugin; other deposits: (1) Klyukvenny, (2) Saku, (3) Pravoingamakitsky, (4) Mylovsky, (5) Rudny, (6) Verkhne–Chineysky, (7) Skvoznoy, (8) Kontaktovy, (9) Luktursky, (10) Unkur, (11) Krasny, (12) Burpala.

The Kodar–Udokan district comprises deposits of black, non-ferrous, noble, and radioactive metals (Figure 2) [2,5,16] formed in the Paleoproterozoic, the most productive era of the concentration of many metals (Cu-Ni magmatic deposits and sedimentary-epigenetic) [31].

2.2. Brief Geology of the Deposits

2.2.1. Deposits in the Carbonate-Terrigenous Rocks

The stratigraphic setting of the Cu deposits is shown in Figure 2. We describe the deposits from the lower to upper levels, i.e., from the Chitkandinsky to the Sakukansky formations as follows: Krasny, Burpala, Unkur, and Udokan. They are characterized by similar structures, i.e., all deposits consist of one or several sulfide-rich horizons concordant with the host rock bedding (mostly, in synclines).

The Krasny deposit takes the lowest position in the stratigraphic sequence of rocks in comparison with the other deposits (Figure 2). It occurs within the Chitkandinsky formation (Figure 3a) consisting of grey fine–medium-grained oligomictic or calcareous sandstones, shales, and siltstones. It is suggested [2,16,32] that these rocks represent the deltaic facies of large rivers. Sulfides form a disseminated ore horizon that extends for 1000 m (on the surface) at a thickness of 200 m and consists of several orebodies.

The Burpala deposit (Figures 2 and 3b) is located in the Sakukansky Formation, in its lower part, consisting of grey medium-grained sandstones and siltstones [32]. The ore horizon extends for almost 9 km at a thickness of around 150 m and lies in line with the sandstones. It comprises several orebodies, the largest of them being 3 and 5 km long and 10–15 m thick (on average) [2,32]. They are located in the exocontact zones of the gabbro–dolerite dykes, rarely, separately (Figure 3b).

The Unkur deposit occurs in the exocontact of the Luktursky gabbro–norites massif (Figures 2 and 3c) among the sandstones of the Talakansky Formation (the Kemensky series of the Udokan complex). There are several ore bodies within the deposit, which were studied mainly using boreholes. The thickness of the ore-bearing horizons is 50–70 m, and the boundaries of the ore bodies are determined using the sampling results; their thickness varies from 20 to 30 m.

The Udokan deposit (Figures 2 and 3d) is the largest in the region (the third place in the world in resources between sandstone-hosted deposits [33,34], it is confined to the Naminginsky brachysyncline; 10 km × 15 km in size, extending north-westwards), and the core is composed of rocks related to the Naminginsky Formation (Kemensky series). The limbs of this fold are composed of the rocks of the Sakukansky Formation. The brachysyncline has an irregular morphology. It is broken by a large gabbro dyke. The orebodies are stratiform or lenticular in morphology with a maximum length of 2–3 km.

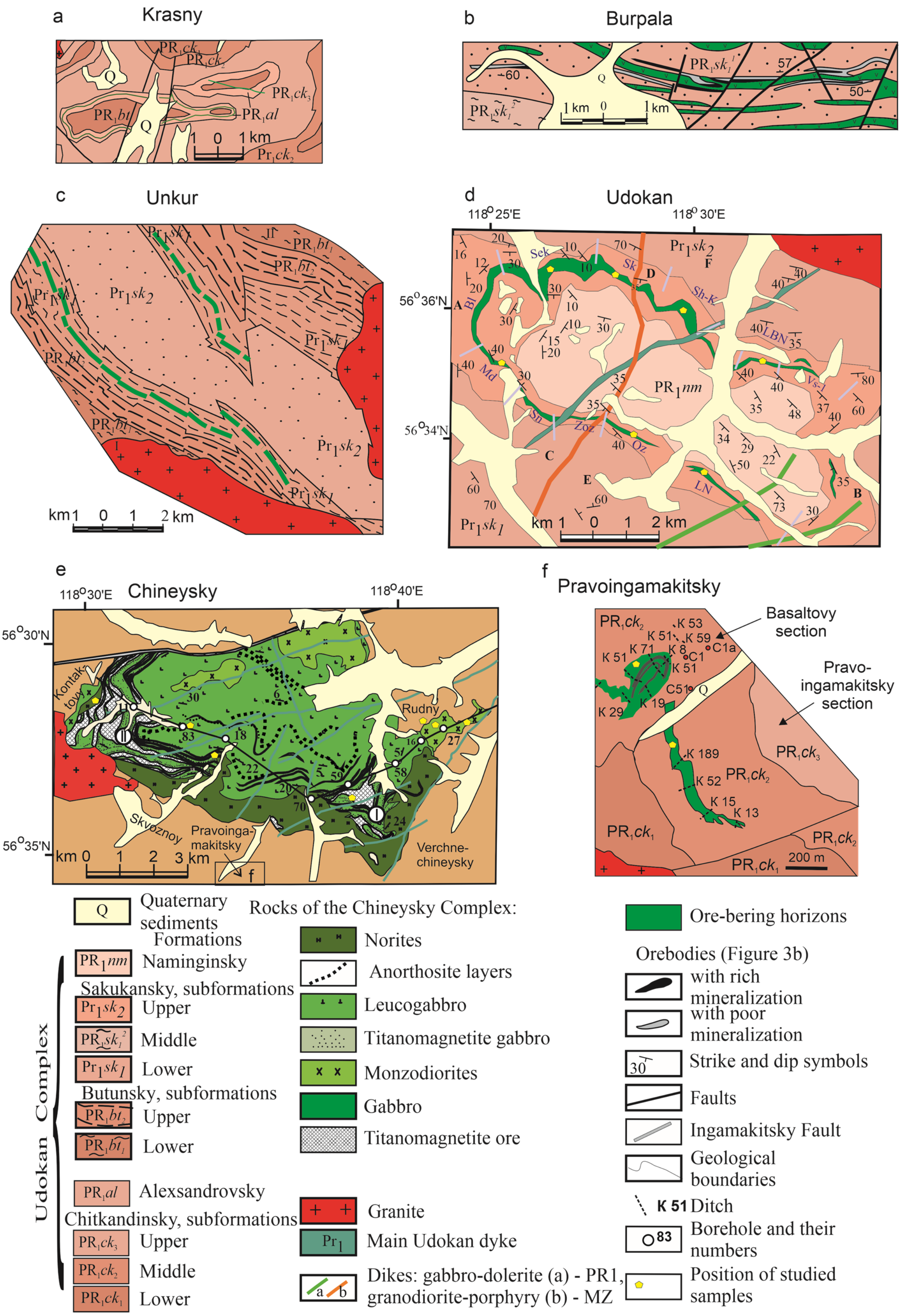


Figure 3. Geological maps of studied deposits: (**a**)—Krasny, (**b**)—Burpala, (**c**)—Unkur, (**d**)—Udokan, (**e**)—Chineysky, (**f**)—Pravongamakitsky. Modified after [4,9,12,15]. Sections of the Udokan deposit: Md—Medny, Bl—Bluzhdayushcy, Sek—Sekushchy, Sk—Skvosnoy, Sck—Skolzky, Sh-K—

Shumny–Krutoy, LBN—Levy Bort Naminga, Vs—Visyachy, Vs1—Vostochny 1, LN—Levaya Naminga, OZ—Ozerny, Zoz—Zaozerny.

2.2.2. Magmatic and Complex Deposits

The deposits of these types are related to the gabbro, gabbro–norites, and anorthosite of the Chineysky complex [8–10].

The Chineysky pluton is the largest layered intrusion that breaks up the rocks of the Sakukansky Formation in the immediate vicinity of the Udokan deposit. Its age according to a study of the U-Pb system in zircons is 1867 ± 3 Ma [35] and according to Ar-Ar data in biotite is 1880 ± 16 Ma [36]. Our SHRIMP-II determinations of U-Pb in zircons for high-titanic gabbro are 1858 ± 17 Ma; the low-titanic gabbro age is 1811 ± 27 Ma [10]. The Chineysky pluton is characterized by different-scale rhythmicity; the thickness of rhythms varies from micro-rhythms (first centimeters to decimeters) to macro-rhythms (first hundred meters). The rock compositions within these units change from pyroxenites or titanomagnetites to leucogabbro–anorthosite. Sulfides, quartz, and mica occur in the upper parts of the micro- and macro-rhythms [9].

The Chineysky pluton comprises titanomagnetite (Etyrko and Magnitny deposits) and sulfide ores (Rudny, Verkhnechineysky, and Kontaktovy deposits) in the central and peripheral areas of the massif, respectively. The sulfide ores are subdivided into endo- and exocontact ores relative to the pluton contact. Their average thickness is 15–20 m and extension is 1–2 km.

The Luktursky massif is very close in composition to the Chineysky pluton [9]. Titanomagnetite and sulfide ores are related to it, as well. It is not well studied as it is poorly exposed at the surface. According to sporadic borehole data, its thickness reaches 1.5 km. The Mylovsky massif is even less exposed on the surface, which is predominantly recorded at depth by geophysical data [9]. It is studied using separate outcrops of gabbro, which also contain titanomagnetite and sulfide mineralization.

The Pravoingamakitsky deposit is located to the southwest of the Chineysky pluton. It contains several sections (Basaltovy, Pravoingamakitsky, Skvoznoy), which differ significantly in ore type—morphology, textural and structural features, and chemical and mineral composition. They are combined into one deposit on the basis of spatial proximity. The orebodies are represented as banded horizons of disseminated Cu mineralization in sandstones of quartz veins with sulfides (1–3 m thick). There are two orebodies in the Basaltovy section consisting of disseminated sulfides in sandstones (7–13 m thick). They are located within an overturned anticline and separated by a subeconomic cupriferous interval. At the same time, quartz veins with sulfide mineralization occur here as well (see photo in "Section 4").

3. Objects and Methods

The material for the research was selected during field trips at the deposits of the Kodar–Udokan region, where rocks and ores were studied in outcrops and cores of boreholes. Textural and structural features of ores were studied under an Olympus microscope, and mineral composition was determined by X-ray microanalysis on JEOL 8200 (JEOL, Tokyo, Japan, at IGEM RAS, analyst V.I. Taskaev). Imaging conditions: accelerating voltage 20 kV, current on Faraday cylinder 20 nA, exposure for main elements—10 s, for impurity elements—20 s. Analytical lines were used: Kα-line (Si, Na, Mg, Fe, Ti, V, Ni, Ca, Al). The analyses of major elements were standardized by minerals of close composition. The ZAF-correction technique was used to calculate element concentrations.

Cu, Co, and Ag were determined by ICP-AES on an Iris Intrepid II XDL (Thermo Electron Corporation, Waltham, MA, USA), with noble metals preparatorily concentrated and analyzed using ETAAS on a SolaarMQZ (Thermo Electron Corporation, Waltham, MA, USA) using the method described in [37] at the Laboratory of the Geochemistry and Analytical Chemistry of Noble Metals at the Vernadsky Institute of Geochemistry and Analytical Chemistry RAS (analysts I.Kubrakova, O.Tyutyunnik).

The isotopic composition of sulfur in small sulfide grains was determined by laser sampling from sulfides mounted in epoxy beads, with measurement of the $^{34}S/^{32}S$ isotopic ratio using The Thermo Fisher Scientific MAT-253 multi-collector mass spectrometer and Isodat Acquisition program in the laboratory of stable isotopes of the FEGI FEB RAS according to the method [38–40]. When exposed to femtosecond ultraviolet laser radiation (New Wave Research), an aerosol was formed on the sample, from which sulfide sulfur in a helium flow was converted into SF_6 gas through the reaction of sulfides with BrF_5 as it passed through a heated reactor. The Faraday cups of the multi-collector allow synchronous measurement of masses 127 ($^{32}SF^{5+}$), 128 ($^{33}SF^{5+}$) and 129 ($^{34}SF^{5+}$). During the measurements (700 s), the sample signal was compared with the standard SF_6 gas signal, which was applied automatically as 4 pulses before and 3 pulses after sample analysis. The laser frequency was 100 Hz, the beam diameter was 100 μm, and the crater depth was about 40 μm on average. The results are presented as $\delta^{34}S$ values relative to the V-CDT standard $\delta^{34}S = [(^{34}S/^{32}S) \text{ sample } /(^{34}S/^{32}S) \text{ std}] - 1$. For the laboratory SF_6 standard, a value of +17.45‰ $\delta^{34}S$ certified relative to IAEA-S-1, IAEA-S-2, IAEA-S-3, and NBS-123 standards were assumed. The precision of the $\delta^{34}S$ analyses was ±0.20‰ (2σ).

Large sulfide grains were analyzed at TSNIGRI (analyst S.Kryazhev). Sulfide mineral powders were analyzed by conventional methods using the techniques of Robinson and Kusakabe [41,42], with the decomposition of sulfide minerals by reaction with CuO at 750 °C, with further isotopic analysis of SO_2. Analytical uncertainty of ±0.2‰ (2 σ) for $\delta^{34}S$ was estimated from internal standards of homogenous pyrite from the Gaiskoe deposit in the Southern Ural ($\delta^{34}S_{CDT}$ = +0.7‰) and sphalerite NBS 123 ($\delta^{34}S_{CDT}$ = +17.3‰).

4. Results

We studied the texture, structure, and mineral composition of the representative samples (62 samples) taken from the main orebodies of the deposits mentioned above. They have similar structures where the sulfide minerals form horizons in the sandstones consisting of layers with different sulfide amounts (Figure 4). This structure is reflected by the Cu minerals in the oxidation zone on the surface of the sandstone (Figure 4a,c,d).

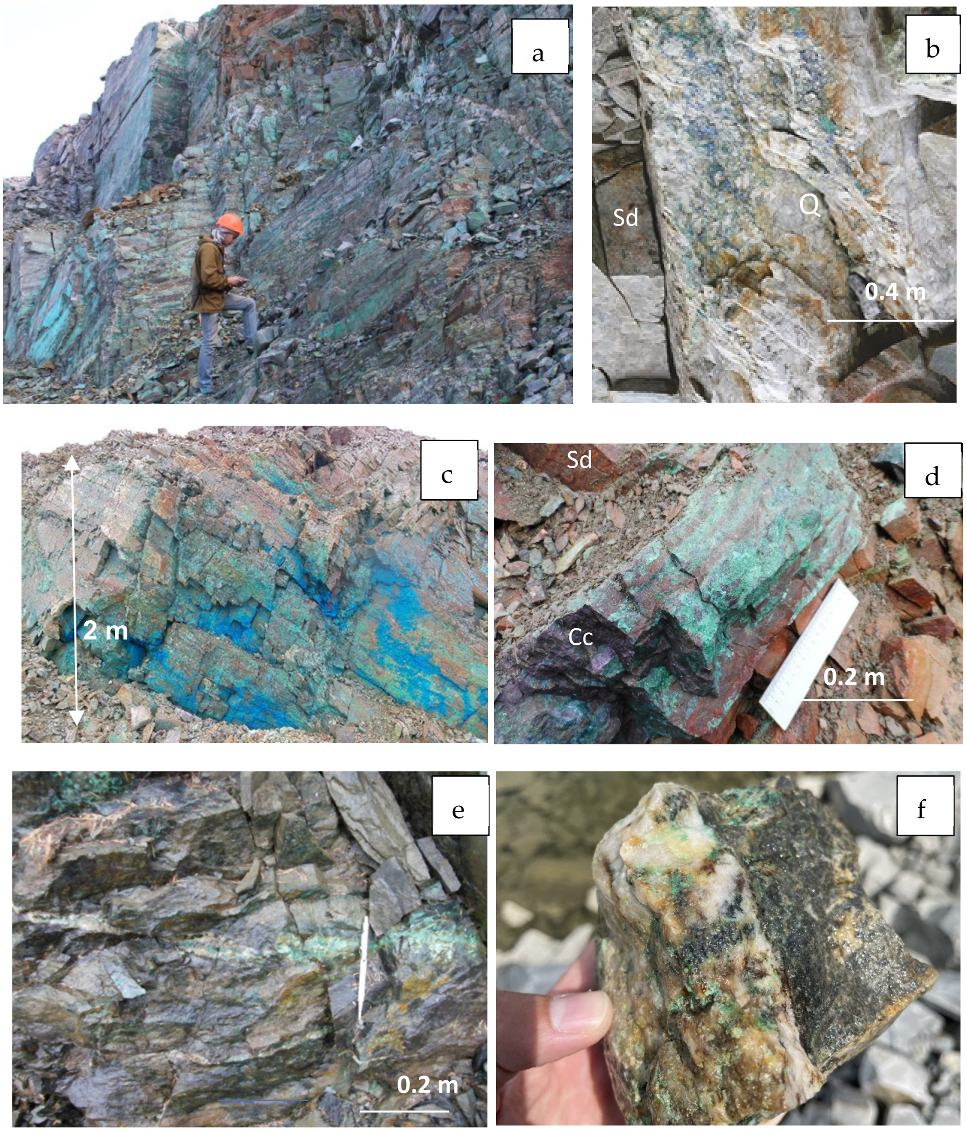


Figure 4. Copper sandstone (**a**,**c**,**d**) and quartz veins with sulfide mineralization. (**a**–**d**)—Udokan deposit, (**e**,**f**)—Unkur deposit. Sd—sandstones, Cc—chalcocite, Q—quartz, and blue and green layers are associated with secondary Cu minerals (chrysocolla, malachite, azurite, etc.).

4.1. Deposits in Carbonate-Terrigenous Rocks

The Krasny deposit is characterized by the most complex chemical composition compared to the other sandstone-hosted deposits [32]. Besides copper (around 1 wt.%), their ores are enriched with Ag (70–250 ppm), As (up to 3 wt.%), Au (0.3 ppm) and contain Bi, Sb, Mo, Co, Pb, Zn, Se, Te, and U. The sulfide ores have a disseminated and fine-grained texture (Figure 5a,b). The mineralogical composition reflects their chemical composition. The main minerals are chalcopyrite, pyrrhotite, arsenopyrite, cobaltite, and magnetite; the rare minerals are pentlandite, millerite, tennantite–tetrahedrite, chalcocite, hematite, uraninite, and Ce–monazite. The secondary minerals are represented by covellite, native Cu, Fe-oxides, malachite, azurite, supergene chalcocite, tenorite, and cuprite. There are some mineralogical types of ore at the deposit, i.e., pyrrhotite, bornite–chalcopyrite, pyrite–chalcopyrite, and arsenopyrite–tennantite–tetrahedrite. They are characterized by enrichment in different elements—Co, Ni; Ag, Au; Bi, Sb, respectively.

The mineral compositions are given in Supplementary Materials (SM,Table S1). The sulfide minerals form grains from 0.2 mm to 2 mm, and their aggregates are up to 2 cm

(Figure 5). Usually, they perform interstitials between silicates. The composition of the main minerals depends on their association. The ore-forming minerals have a composition very close to stochiometric (Table S1, Nos 17-21). The minor ore minerals are sphalerite, galena, and cerussite. Chalcopyrite in the aggregates with bornite contains Ag (up to 0.03 wt.%) while the same mineral in association with pyrite is enriched in Co (0.04 wt.%). Pyrite constantly contains an admixture of cobalt (0.04–0.19 wt.%), less frequently nickel (up to 0.29 wt.%), and sometimes arsenic (0.32 wt.%). High Ag (0.17 wt.%) contents were determined in the bornite (Table S1, No 3, 4).

The mineralogical diversity of the ores of the Krasny deposit is also reflected in the sulfur isotopic composition (Table S2; points of analyses are shown in Figure 6). A wide range of $\delta^{34}S$ characterizes its mineral associations varying from −8.1 to +13.5‰ (n = 13). This may be due to several reasons: both the formation of sulfides from different sources (hydrothermal, magmatic, etc.) and the superimposed processes. However, the ores of this deposit are the least susceptible to secondary alterations; therefore, different primary genesis is the most probable reason for them.

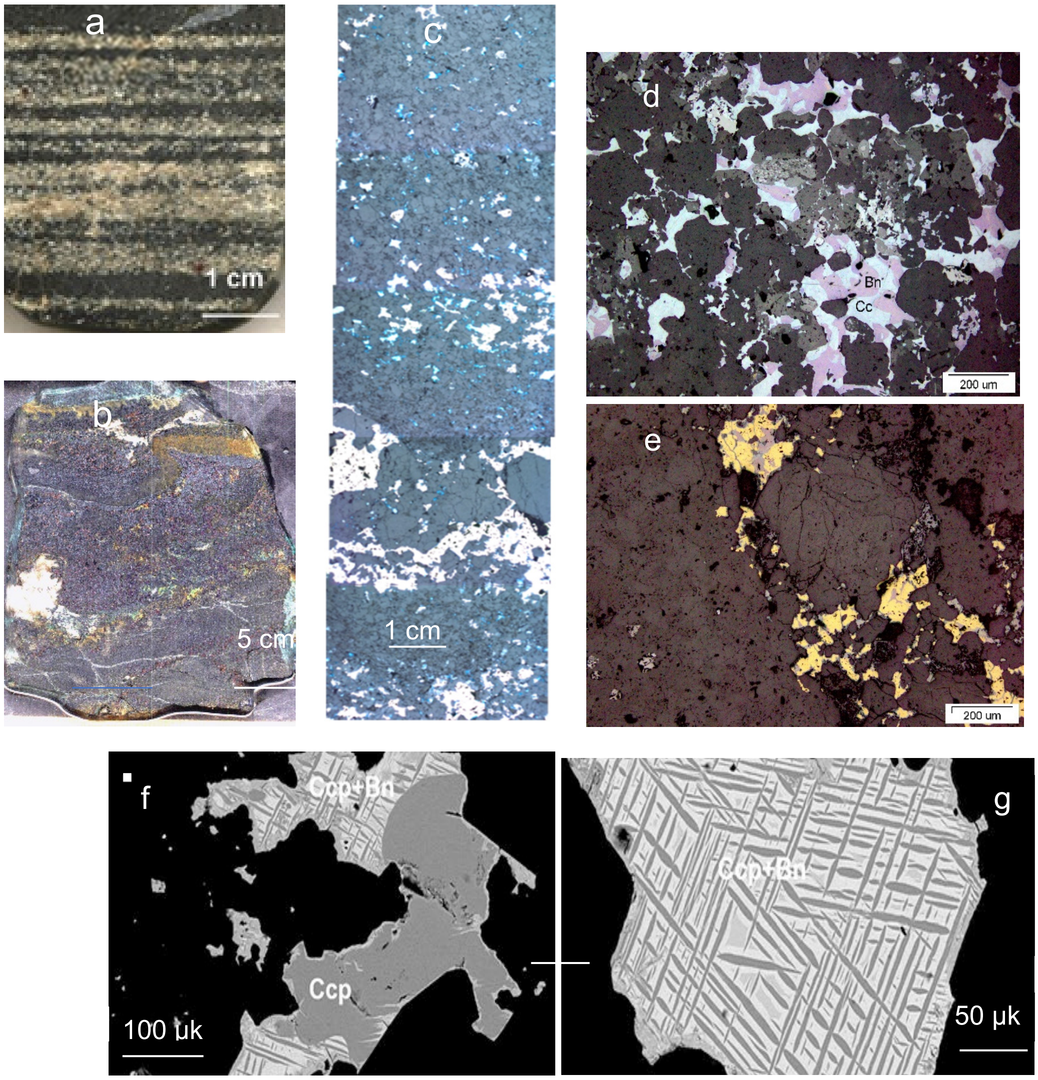


Figure 5. Texture of the copper ores at the Krasny (**a**) and Udokan (**b**–**e**) (polished samples), and BSM images (**f**,**g**) of chalcocite–bornite grains (Ccp and Bn, dark gray—chalcopyrite; light gray-bornite), Udokan deposit.

The Burpala deposit includes two major ore layers and some lens-like orebodies. It contains around 1.25 wt.% Cu, 50 ppm Ag, and 0.1 ppm Au (on average), while the highest

Ag concentrations were determined in the chalcocite–bornite ore where they reach up to 125 ppm. The Ag contents in the pyrite–chalcopyrite ore are much less; they are only 25 ppm. There is a strong Ag-Cu correlation in the ores (Figure S1). In general, the ore minerals have the following relationships—bornite:chalcopyrite:chalcocite as 5:5:1.

The first orebody consists mostly of bornite and chalcocite. Its copper mineralization is characterized by zonation from the bottom layer to the top, where the chalcocite–bornite ores are replaced primarily by bornite, then by chalcopyrite, and finally by pyrite. The second orebody is represented by mainly chalcopyrite and pyrite.

The sulfur isotope composition demonstrates a narrow range of values. In this study, we obtained only two analyses $\delta^{34}S = -10$ and -11‰ (and two samples were studied earlier that demonstrated the values $\delta^{34}S = -16$ and -11‰).

The Unkur deposit is characterized by low Cu (0.75 wt.%) content but, at the same time, by high silver content (70 ppm; 5 times higher than in the Udokan deposit). It consists of two ore horizons located mostly in the fine-grained sandstone with hematite, magnetite, and ilmenite. Besides these ore minerals, the rocks contain Cu minerals, i.e., chalcopyrite, bornite, pyrite, and a few chalcocites. The rare minerals are native Ag, acanthite Ag_2S, native Au, Pd phases, and uraninite. The texture of the ore is disseminated, rarely massive in small lenses. The zonation of the typical orebodies is as follows: the bottom is enriched in chalcopyrite and pyrite while bornite dominates at the top. The zone of oxidation comprises Cu carbonate and sulfate, i.e., malachite, azurite, antlerite, and chrysocolla.

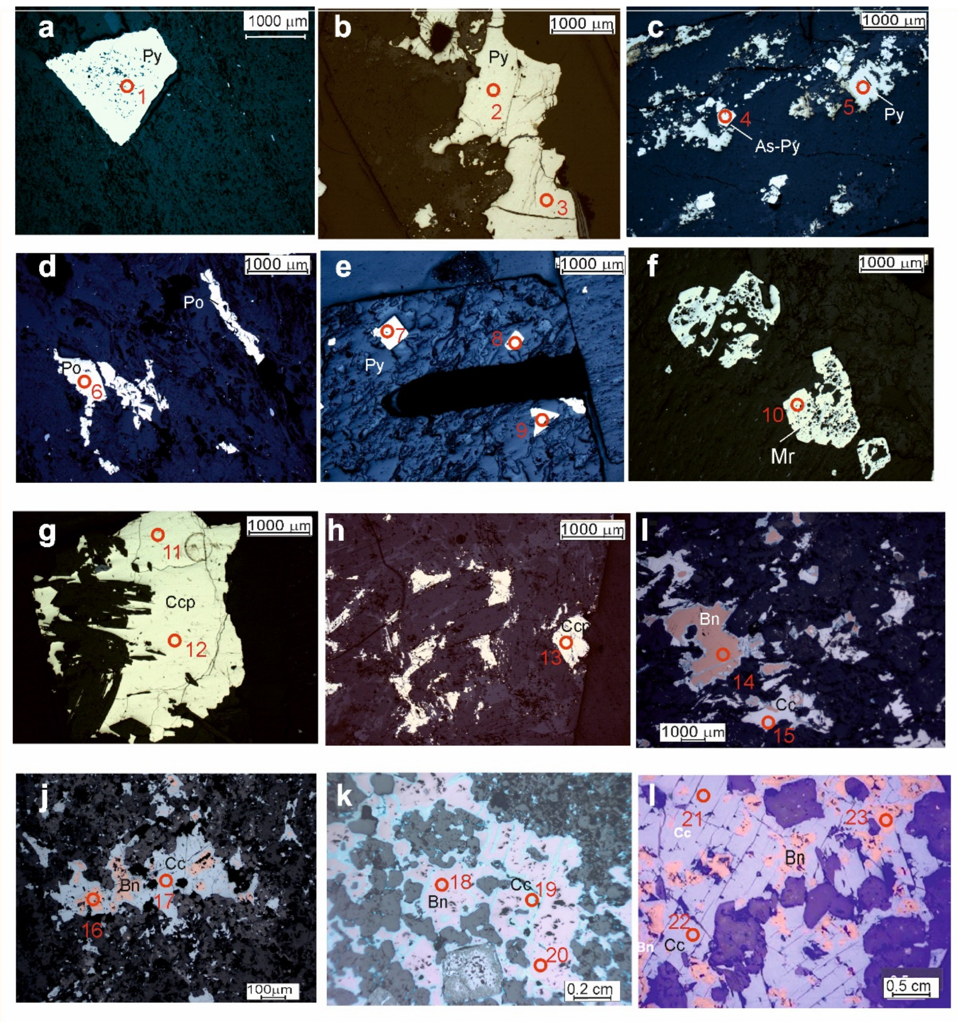


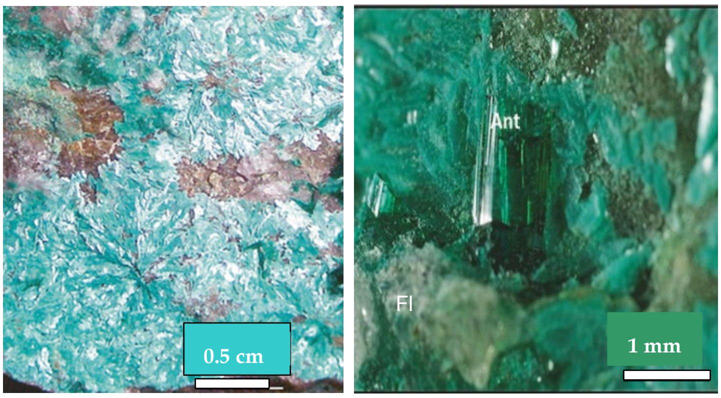
Figure 6. Photomicrographs of sulfides with points of Laser isotope analyses. Number of points corresponds to the number of analyses in Table S2. Minerals: Py—pyrite, Ccp—chalcopyrite, Cc—chalcocite, Bn—bornite, As-Py—arsenopyrite, Mr—marcasite. Deposits: (**a**–**h**)—Krasny, (**i**–**l**)—Udokan.

The Unkur deposit contains sulfides characterized by very different sulfur isotope compositions. The $\delta^{34}S$ data are −9‰ for bornite and +11‰ for chalcopyrite (Table S2).

The Udokan deposit has elevated Cu content (1.45 wt.%) in comparison with the other sandstone-hosted deposits but low Ag (11–13 ppm on average). At the same time, it comprises huge Fe resources. Many trace elements occur in the ores including Au, Co, Pb, Mo, and V. The sulfide ores are characterized by a disseminated texture (Figures 5 and S2), and in some places they are massive. The latter texture is typical of small lenses. Often the disseminated ores are changed gradually by the massive ores in the vertical sections. Bornite–chalcocite ores dominate the deposit. Pyrite–chalcopyrite mineralization is subordinate and located at the lowest levels of the deposit. This association forms chalcopyrite–pyrite veinlets, often vertical, in the sandstone.

The rare minerals are cobaltite, native Ag, Ag_2S, native Au, and valleriite. The exsolution textures are typical of a chalcopyrite ore. The bornite–chalcocite ore contains many magnetite grains—crystals or their fragments. The chalcocite usually forms rims around the bornite. The morphology of these aggregates depends on the morphology of the interstitial space (Figure 6). The composition of the ore minerals from the Udokan deposit is given in Table S1. The chalcocite (and djurleite) contains Fe [43].

The Udokan deposit is characterized by a large zone of oxidation, especially at the surface, where it contains 50 vol.% of the total ore volume. This zone pinches out to depth, where it is related to thick fractures and faults. Therefore, the zone of oxidation plays a very important role in the ore balance. It consists of minerals of different classes: sulfates (brochantite, antlerite, and chalcanthite), carbonates (malachite, azurite, and cerussite), silicates (chrysocolla), and Fe-oxides (goethite and hydrogoethite) [44–48]. Two rare phosphates were found, i.e., a new mineral named krendelevite (proximate composition $CuAl(SO_4)(PO_4)(OH)\cdot H_2O$) and fluelite [10,49] (Figure 7a,b).



(**a**) (**b**)

Figure 7. Minerals from the zone of oxidation: (**a**)—krendelevite, (**b**)—antlerite and fluellite.

In general, the sulfur isotope composition of the sulfides in the Udokan deposit varies significantly. It does not depend on a geological setting of samples taken within different sections of the deposit (Medny, Sekuschy, Shumny–Krutoy, etc., Figure 3, Table S2). These variations are due to different mineral associations and their origin, i.e., typical chalcosite–bornite ores are characterized by $\delta^{34}S$ = −2.7%–16.0‰, while chalcopyrite–pyrite ores have very light S-isotope composition, where $\delta^{34}S$ changes from −15 to −28% (Table S2 [50–53]), and the cross-cutting chalcopyrite–pyrite veinlets are close to −13‰. Some samples located nearby to the gabbro dyke have positive $\delta^{34}S$ (+4 and +13‰–+14‰) [50].

4.2. Deposits in Magmatic Rocks and Other Deposit Types

The most important object of these types is the Chineysky pluton with several sulfide sections (or separate deposits) in its contact zone with the rocks of the Udokan complex (Figure 3e) including the Rudny, Kontaktovy and Verkhnechineysky deposits. The first two deposits have the most important economic value. They are characterized by the sulfide occurrence in the magmatic rocks (gabbro, titanomagnetite gabbro, gabbro–norite, gabbro–diorite) and in the exocontactic zone under the lower pluton surface. Similar mineralization was found in the Luktursky and Mylovsky massifs, which gabbro comprises along with sulfide ore titanomagnetite mineralization. The Pravoingamakitsky deposit is characterized by features of different genetic types of ores.

The Chineysky pluton comprises different types of mineralization that were described in [8–10]. Here, we give their brief characteristics and new data on mineral and S-isotope compositions (Table S1)

The distinguishing feature of the sulfide mineralization at the Chineysky pluton is a high Cu content (Cu/Ni = 10–100) compared to the other Cu-Ni deposits, where the Cu/Ni ratio is < 1, as a rule. The elevated Co content is typical as well; in general, Cu:Ni:Co = 76:7:1; Pd/Pt = 4-3 (maximum Pt + Pd content is 355 ppm) [8]. The average contents of Cu and Ni at the Rudny deposit are 0.7 and 0.05 wt.%, respectively; the noble metals have the following contents: Pt and Pd are 0.3 and 1.3 ppm, 3.5 ppm Ag, and 0.2 Au. The other deposits of the Chineysky intrusion are poorer than Rudny.

According to geological setting, mineral composition and texture, five types of mineralization were recognized: (1) disseminated sulfides (up to 15%) in layered titanomagnetite ores; (2) endocontact-disseminated sulfides (pyrrhotite–chalcopyrite) in gabbro–norite, gabbro–diorite, and monzodiorite; (3) endocontact-disseminated sulfides in leucogabbro (pyrite–chalcopyrite); (4) exocontact-disseminated sulfides (chalcopyrite) in the sandstone; (5) veins and lenses (chalcopyrite, bornite–chalcopyrite) of massive sulfides in the sandstone (Figure 8c,d). The first type occurs in the center of the pluton (Etykro), the second, the third, and the fifth ones are localized in its eastern part (Rudny), the fourth type is related to the western part of the pluton (Kontactovy).

The sulfide mineralization in the titanomagnetite ore does not have economic value but sometimes is characterized by elevated metal concentrations (for example, Pt content reaches up to 1.8 ppm). It consists of pyrrhotite, chalcopyrite, pentlandite (according to their volume in rocks), and sometimes pyrite. Pyrrhotite is represented by hexagonal and monoclinic verities and throilite. High Co content occurring in pentlandite is typical of this mineralization (up to 18 wt.%) (Table S1, No 23,24; [10]). Cobaltite, linnaeite, gersdorffite, sphalerite, galenite and other minerals often take place in this ore.

Disseminated ores occur in the endocontact zones in the Rudny (Figure 9) and Kontaktovy deposits. They differ in mineral composition: the first one consists of pyrrhotite and chalcopyrite in varying ratios while the second ore has a chalcopyrite–pyrite composition. Minerals of the linnaeite group and cobaltite–gersdorfite range occur very often in disseminated ores forming large aggregates (3 cm) and veinlets. Among the rare minerals, the Pd-Bi-Te-Sb group dominates (sobolevskite, sudburyite, froodite, kotulskite, michenerite, stibiopalladinite, and isomertieite) [54].

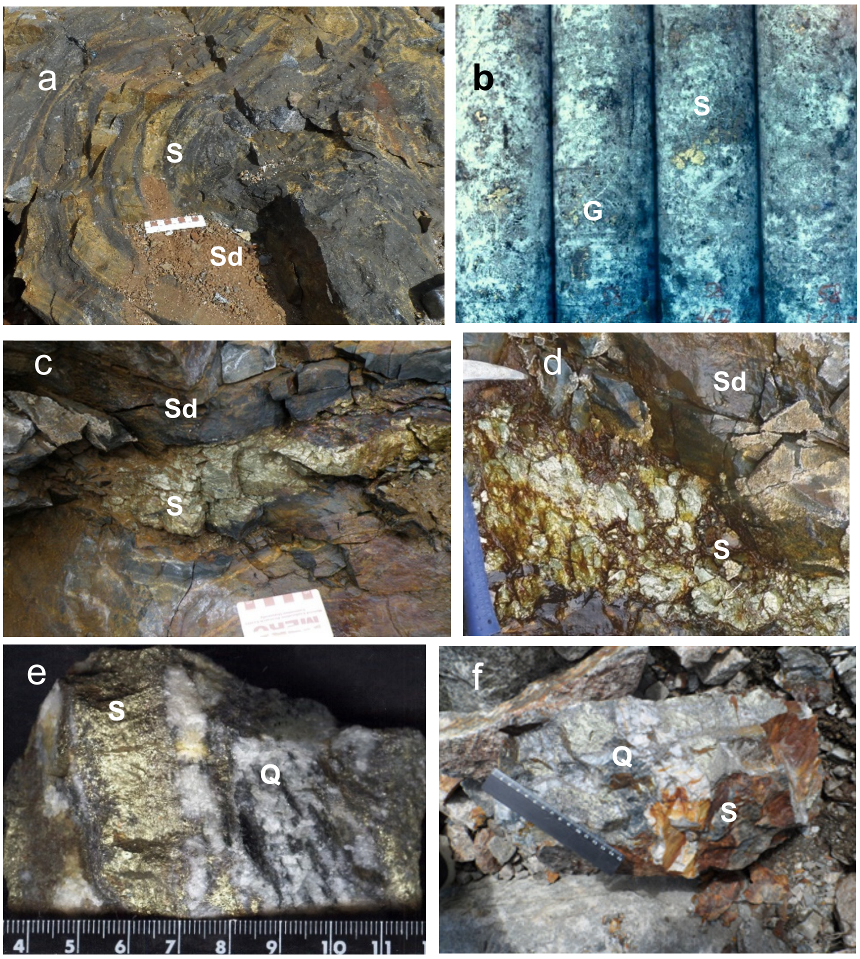


Figure 8. Sulfide ores at the Chineysky (**a**–**d**) and Pravoingamakitsky (**e**,**f**) deposits. S—sulfides, Q-quartz, Sd—sandstone, G—gabbro.

Veins and lenses consisting of chalcopyrite are located along the lower pluton contact, 5–20 m from it. They have massive texture (Figures 8 and 9), and frequently their zalband is enriched in Ni concentrated in millerite. Co and Ni arsenides and sulfoarsenides present in the veins. The pentlandite of this ore type is characterized by low Co content (2–3 wt.%).

We analyzed $\delta^{34}S$ both in the single grains using the laser ablation method (Figure 10) and in the bulk sulfides; the data are similar. The $\delta^{34}S$ values vary within a narrow range: from +0.5 to +4.7‰; only three values are 7.2‰–7.5‰ (Table S2; Figure 10).

The Lukturksy deposit is situated in the Chara trough. It comprises titanomagnetite and sulfide mineralization, which take place in the coarse-grained gabbronorite and norite. The 34-borehole penetrated the sulfide-bearing rocks in the upper part of the Luktursky pluton [9]. The ores mostly have a disseminated texture. The sulfides consist of 10–15 vol.%, although sometimes they take up to 30 vol. %. They are characterized by a high Ni content in comparison with the mineralization of the Chineysky pluton; therefore, the Cu/Ni ratio changes from 0.5 to 0.8. The ores contain 2 ppm Pd, 0.9 ppm Pt, 4.2 ppm Ag, and 0.1 Au. Chalcopyrite, pyrrhotite, and pentlandite are the major minerals. The last one has low Co concentrations (<2 wt% Co). Pyrite is a subordinate mineral. Most minerals have $\delta^{34}S$ = 0.6‰–3.9‰ and only one analysis was 6.3‰ (Table S2).

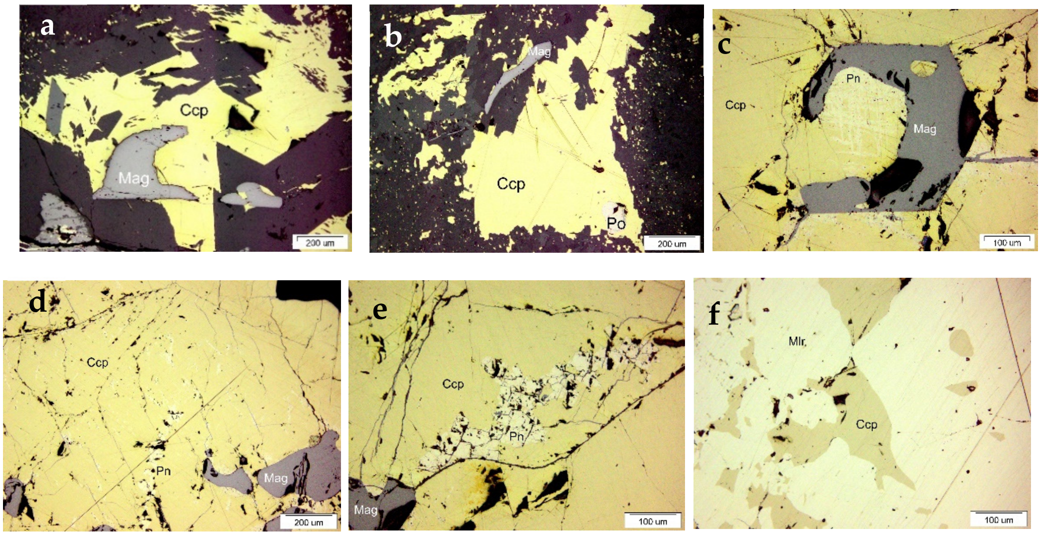


Figure 9. Sulfide ores of the Chineysky pluton: (**a**,**b**)—disseminated chalcopyrite ore in gabbronorites; (**c**–**f**)—vein of massive chalcopyrite ore: (**c**)—chalcopyrite ore with pentlandite near magnetite, (**d**,**e**)—veinlet of pentlandite in chalcopyrite, (**f**)—replacement of chalcopyrite with millerite. Minerals: Ccp—chalcopyrite, Pn—pentlandite, Mag—magnetite, Po—pyrrhotite, Mlr—millerite.

The Pravoingamakitsky deposit is the most complex deposit in the region because it comprises very different ores concentrated at the Skvoznoy, Pravoingamakitsky proper, and Basaltovy sections (Figure 3). In general, the concentrations of the metals are as follows: 0.9 wt.% Cu, 25 ppm Ag. Nevertheless, they change dramatically within different ore bodies from 0.3 to 30% (in the chalcopyrite ore). The ore of the Skvoznoy and Pravoingamakitsky deposits are partially similar to the exocontact ore of the Kontaktovy deposit; they have a pyrite–chalcopyrite composition.

The Skvoznoy deposit is similar to the typical Ni-Cu mineralization in nickel enrichment. The sulfide ores also contain high amounts of Au, Ag, and PGE (Table 1). The highest PGE grade (Pd/Pt ~3–4) typically occurs in the massive ore. In contrast, the average concentrations of Pd and Pt in the disseminated sulfide are ~2 and ~0.5 ppm, respectively.

The Basaltovy section is different because it comprises quartz veins with chalcopyrite mineralization enriched in PGE [22]. The major ore minerals in this section are characterized by high concentrations of Ni and Co. For example, their concentrations in pyrite are 1.75 and 1.48 wt. %, respectively. These ores contain many rare minerals (up to 10 μm) such as clausthalite $Pb_{1.00}(Se_{0.78}S_{0.22})_{1.00}$, bravoite $(Ni_{0.73}Fe_{0.30})_{1.03}S_{1.97}$, hessite $Ag_{1.98}Te_{1.02}$, bogdanovichite $AgBiSe_2$, and palladium intermetallides, the composition of which could not be determined precisely due to their small size (a few micrometers).

Earlier, we studied the fluid inclusions in the quartz from the quartz–sulfide veins [22]. It was demonstrated that two-phase inclusions homogenized into the liquid phase (at T = 222–192 °C) and contain an aqueous solution with a salt concentration of 2.7–2.6 wt. % NaCl equiv. Sodium and magnesium chlorides are the main components in these inclusions (temperature of eutectic changes from –43 to –38 °C). We studied the sulfur isotope composition in the sulfides from these veins; $\delta^{34}S$ varies from −2.9 to +7.0‰ and is similar to the magmatic minerals at the Chineysky deposits.

Table 1. Mineral and chemical composition of the deposits in the Kodar–Udokan region.

Deposit	Section	Ore Composition	Subordinate and Rare Minerals	Cu, wt.%	Ag, ppm	Co, ppm
Luktursky		Chalcopyrite–pyrrhotite–pentlandite	Millerite, etc.	0.5	4.2	15

Chineysky	Rudny	Pyrrhotite–chalcopyrite	Pentlandite Cobaltite Gersdorffite Sperrylite, Michenerite, etc.	0.7	3.5	20
	Kontaktovy	Pyrite Chalcopyrite	Pyrrhotite, Pentlandite, etc.	0.6	-	18
Udokan	Sekuchshy	Chalcopyrite Chalcocite Bornite Pyrite	Djurleite, Digenite Anilite, Covellite Acanthite, Native Ag, Cobaltite, Betekhtinite, etc.	1.94	191	4
	Shumny–Krutoy	Pyrite Chalcopyrite	Bornite	1.08	80	30
Unkur		Pyrite Chalcopyrite Bornite Chalcocite	Uraninite Stromeyerite Mercury Balkanite Naumannite Allanite Thorite	0.8	22	600
Burpala		Pyrite Chalcopyrite Bornite	Chalcocite Galena	1.63 3.0	26 125	210 14
Pravoingamakitsky	Skvoznoy	Pyrite Chalcopyrite				
	Basaltovy	Pyrite Chalcopyrite	Hessite, Clausthalite, Bravoite, Bogdanovichite	5.0	4.2	24
	Pravoingamakitsky proper	Chalcocite Bornite	Chalcopyrite, Pyrite, etc.	1.42	60	30
Krasny		Pyrite Chalcopyrite–Pyrrhotite	Bornite, Arsenopyrite Tennantite Tetrahedrite, etc.	1.15	37	72

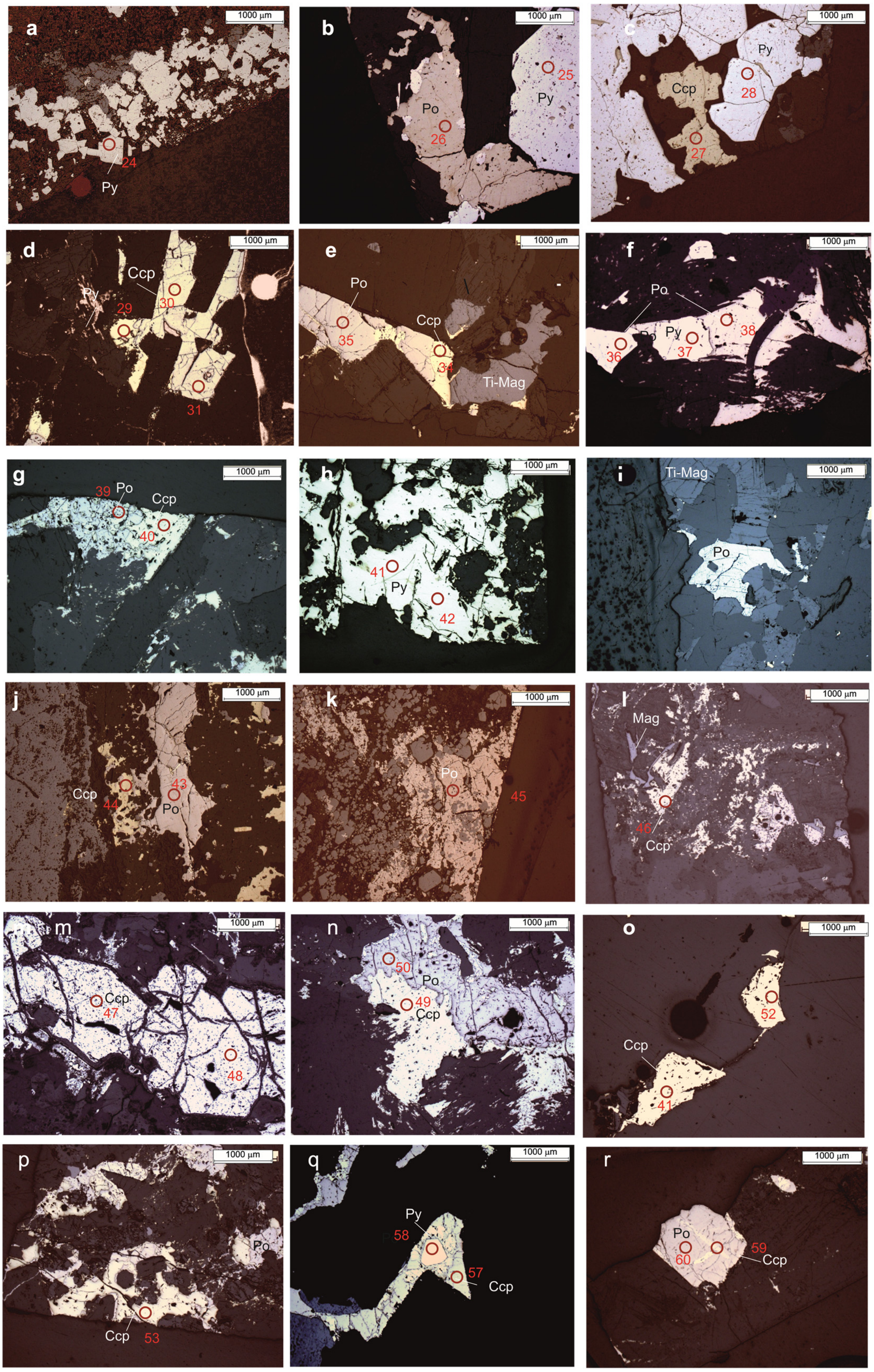


Figure 10. Photomicrographs of sulfides with points of Laser isotope analyses. Number of points corresponds to the number of analyses in Table S2. Minerals: Py—pyrite, Ccp—chalcopyrite, Po—pyrrhotite. Deposits: (**a**–**n**)—Chineysky, (**m**–**r**)—Luktursky.

5. Discussion

5.1. Short Overview

The genesis of extra-large deposits is a special problem of geology [55–58], considered both in the field of ore genesis, petrology, sedimentology, and geochemistry, as these deposits represent giant anomalies of elements in the Earth's crust. There are some special conferences that were devoted to this problem, for example, the 13th Quadrennial IAGOD Symposium (Adelaida, 2010) had the title "Giant Ore Deposits Down-Under" [59,60]. The main problem is whether giant deposits are the result of special geological processes or whether they were formed under normal conditions. Among them, sediment-hosted Cu deposits take an important place in the world market because they supply around 30% of the Cu. They are related to stratigraphic units (i.e., they are stratabound) [61–65] within continental rift zones. Supergiant stratiform reservoir copper mineralizing systems are known in the Paleoproterozoic (Kodar–Udokan Basin), Neoproterozoic (Katanga Basin, Central African Copperbelt), and Permian Zechstein Basin of Europe (Kupferschiefer) [66–68]. Ideas about their origins have changed over the several decades of their study from the 1930s. There are some hypotheses, which can be roughly divided into syngenetic (synsedimentary) and epigenetic (post-sedimentary), regulated by surface and deep processes, correspondingly. The first theory suggests the destruction of ancient copper deposits, the transport of sulfide material, and its deposition in depressions [69]. The second concept proposes an important role of hydrothermal ore fluids deriving from a distant magmatic source that may have entered the sediment basin [22]. The most popular idea on the origin of the sedimentary-hosted Cu deposits is a circulation of ore brine in the red-bed/greybed package [66]. It is related to the geodynamic evolution of the lithosphere as well [70].

All these ideas are reflected in the genetic models of the Udokan deposit. The Kodar–Udokan region contains not only separate unique deposits but, in general, it is enriched with copper, which concentrates in different ore types. Its source, mechanisms of concentration, and deposition have been discussed for many decades [1,10,14,25]. As was shown earlier, the deposits of the Kodar–Udokan region form a wide range of objects varying in geological structure and ore geochemistry. Their locations take place within a 7–8 km-thick sequence of the carbonate-terrigenous rocks of the Udokan complex formed for 30 Ma (Figure 11). The ore composition varies in this vertical section. The sedimentation, hydrothermal, and metasomatic-hydrothermal ore origins were suggested [16,69].

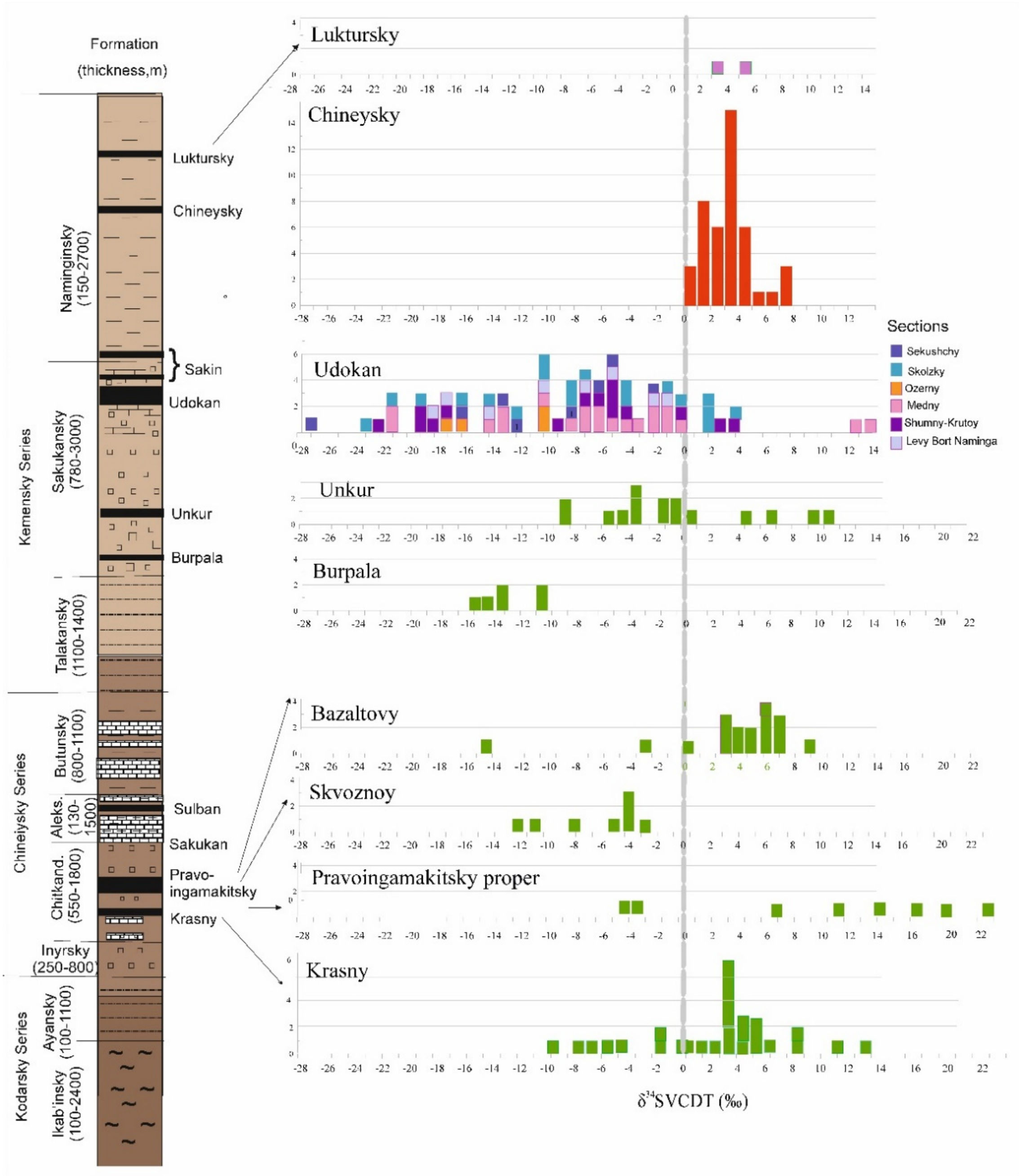


Figure 11. Isotope composition of sulfides in the deposits of the Kodar–Udokan region. Data in Table S2 and after [2,25,50,52].

5.2. Mineral Composition of Ores in the Kodar–Udokan Region

The ores of all deposits in sedimentary rocks have stable composition: they are mainly formed by a chalcocite–bornite association, and, less frequently, they have a chalcopyrite–pyrite composition. This composition is typical of the other copper deposits around the world. Nevertheless, clear differences in the mineral composition of the ores of the different deposits in the sedimentary rocks in the Kodar–Udokan region were established. First of all, the Krasny deposit differs from the other ones due to its unusual composition and many rare minerals, not typical of the Cu sandstone-hosted deposits. It comprises pentlandite, millerite, and tennantite–tetrahedrite, i.e., high-temperature minerals that usually characterize magmatic and hydrothermal ores. Maybe, this is the influence of the Luktursky gabbro massif. Therefore, this composition could be the result of the action of deep magmatic fluids because this deposit is characterized by the lowest setting in the stratigraphic sequence. The Pravoingamakitsky deposit is the most complex because it comprises stratabound ores, disseminated ores, and veins. It occurs in the exocontact of the Chineysky pluton and it is natural to suppose that its ores were largely formed under its influence.

The Udokan deposit has a mineral composition typical of the other sediment-hosted Cu deposits. Djurleite, digenite, and anillite occur in the Udokan chalcocite–bornite ore; covellite was found as well. Rare minerals are represented mainly by silver minerals, as the ores have elevated silver content in almost all deposits. These data are given in Table 1, compiled using our data and the results from Trubachev [19]. Cobaltite often takes place in ores because they contain elevated Co contents. A detailed description of the Ag minerals is given in [71]. Very often, minerals of radioactive elements occur in ores, such as uraninite, torbernite, etc. [10,53]. These features are typical of the Unkur and Burpala deposits as well [72]. Thus, there is a tendency for ore mineral variations in vertical sections (reflecting their geological settings), i.e., from bottom to top.

Magmatic deposits, especially related to the Chineysky gabbro–anorthosite pluton, despite their similarities with other magmatic deposits, are characterized by specific features: Cu minerals dominate in the ores, very often the ores consist of only chalcopyrite and bornite and do not comprise Ni minerals. This suggests its genetic affinity with sedimentary deposits and common Cu sources, although many Co and PGE minerals were found in the ores [10,54].

5.3. Sulfur Isotopes in the Ores of the Deposits from the Kodar–Udokan Region

The problem of the sulfur source in the deposits is no less important than the metals [73,74]; all ores of the district are composed of sulfides. As a rule, the interpretation of its origin is largely based on the sulfur isotope data. Three main sources of sulfur have been distinguished: magmatic, marine water, and evaporites. As usual, their mixing is suggested in the ores. In fact, multiple processes overlap and participate in shaping the final sulfur isotope composition of the ores.

Figure 11 demonstrates the variations in $\delta^{34}S$ at the deposits of the Kodar–Udokan region located at different stratigraphic levels, i.e., from the Chitkandinsky formation to the Naminginsky formation. In general, the deposits are characterized by a significant range of $\delta^{34}S$ values. There is a tendency for the average sulfur values to shift from positive $\delta^{34}S$ to negative ones from the bottom to the top of the section (excluding the Chineysky deposits). The extreme members of this series are the Krasny and Udokan deposits. The first of them is characterized by mainly positive $\delta^{34}S$ values, while the latter mostly has negative values. The Skvosnoy and Unkur deposits take intermediate positions in this range.

Negative $\delta^{34}S$ values are only characteristic of the Burpala deposit, while positive values prevail for the Pravoingamakitsky deposit with quartz–sulfide veins ($\delta^{34}S$ = −2–+7‰.). These differences generally correlate with variations in the mineral composition of the ore-related deposits and evidence complex S sources for them. Hydrothermal fluids, according to the $\delta^{34}S$ data on the quartz–sulfide veins and sulfide veins in exocontact of the Chineysky pluton, are enriched with heavy sulfur isotopes of up to +7.4. The highest datum belongs to the arsenopyrite–pyrite association of the Krasny deposit—+13.5‰. Therefore, we suggest that these fluids (mixed magmatic and groundwater?) participate in the ore formation.

The Udokan ores have mostly negative sulfur isotope data with some exclusions [50–53]. The chalcocite–bornite ores have the $\delta^{34}S$ values = −20‰–−24‰ (Table S2, [10]), while the chalcopyrite–pyrite ores of the Udokan deposit are enriched in light sulfur isotopes of up to $\delta^{34}S$ = −27.2‰ [50] (Figure 11), which is characteristic of the pyrites of the Naminginsky section (borehole 928, 405 m depth), while the disseminated chalcopyrite–pyrite ores of the Medny section have values of −12.9‰. One of the possible processes leading to this composition is a biogenic process of sulfate reduction, which leads to the most significant isotope fractionation. Indirect evidence of the activity of anaerobic bacteria (*Thiocapsa* *thiozimogenes*) occurs in rocks enriched with high C_{org} in the Ikabiysky and Ayansky formations [75]. Of course, the $\delta^{34}S$ shift could be caused by other factors: mixing of different water compositions, fractionation of fluids as a result of temperature changes, etc.

This isotopic composition of sulfides is a typical characteristic of copper sandstone-hosted deposits. Figure 12 shows a distribution of sulfur isotopes in the world-class deposits: Udokan, Katanga Copperbelt, Djezkazgan, and Zechstein. The first two deposits are characterized by a similar distribution of S isotopes, while the ores of the other two deposits are homogenous and depleted in $\delta^{34}S$. Despite the close $\delta^{34}S$ in the sulfides, the first two deposits could be diverse in origin because there is an important difference in their structure, i.e., the Udokansky complex lacks evaporites, while they occur in the Katanga deposits [76,77]. This feature does not allow us to assume brines as a source of sulfur at the Udokan, as is allowed in many models [78–81].

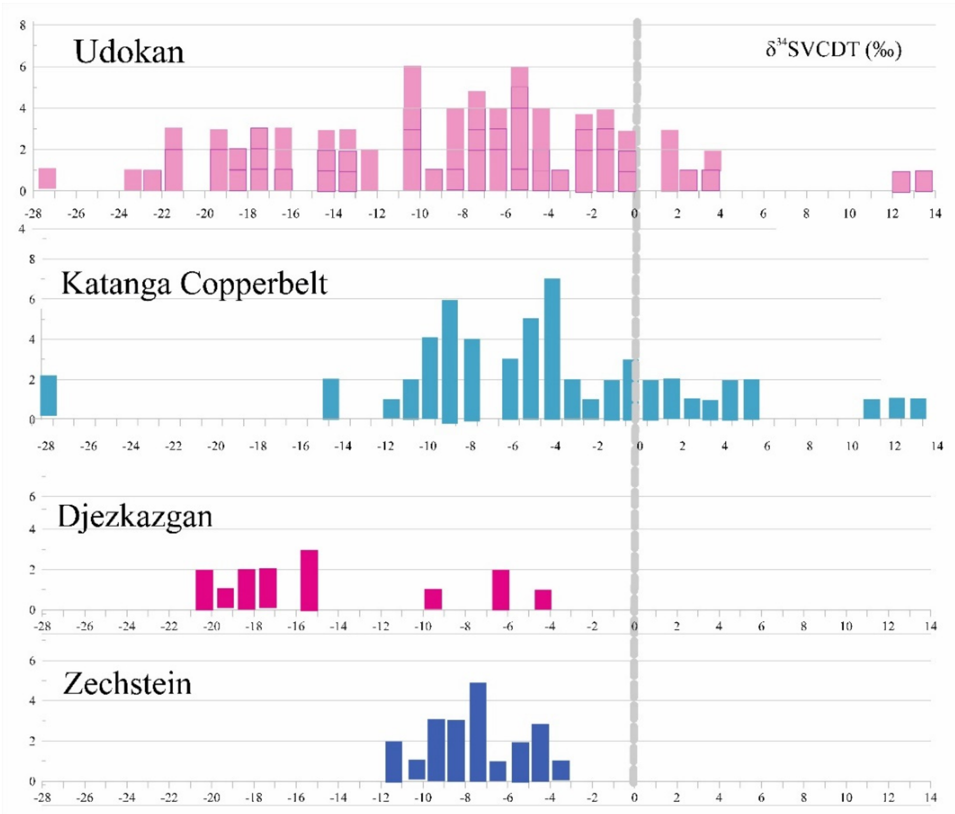


Figure 12. Isotope composition of sulfides in Cu sandstone-hosted deposits. Data in Table S2 and [51,77,78].

5.4. Possible Scenario of the Deposit Formation in the Kodar–Udokan Region

Despite numerous arguments in favor of one hypothesis of ore origin or another one, the sources of the copper and sulfur in them remain unclear. This is especially true for the widespread model of brines in red-colored rocks [33,66]. In fact, neither evaporites, neither red-colored strata were found in the Kodar–Udokan region. Despite the statement about the loss of reddish-colored strata as a result of metamorphism in the Kodar–Udokan area [82], it remains the level of assumption. The contrasting packs (oxidized and reduced) are identified on the basis of the modern composition of the strata, which have already been significantly altered by superimposed processes (metamorphism). A natural question arises: how much do they correspond to the primary composition and can they be used to estimate redox conditions? Therefore, exogenous sources of sulfur and copper remain hypothetical: they could be seawater, red beds, etc.

Meanwhile, endogenous sources could play a significant role in the deposits' formation, which has been increasingly confirmed. The tectonic position of the Cu sandstone-hosted deposits evidences this suggestion. In 1984, Annels [83] proposed linkages between stratiform copper deposits and Neoproterozoic continental rifting (Zambian Copperbelt), taking into account variations in lithological facies and igneous contributions from the mantle sources of major and trace metals. These features are characteristic of almost all copper sandstones: they are confined to rift zones characterized by a reduced thickness of the crust and elevated Moho boundary [11,70]. Therefore, it is quite logical to assume the participation (direct or indirect) of ultrabasic–basic rocks in the deposits' formation. These rocks are characterized by elevated copper contents [84]. For the lower crust the concentration was estimated as 90 ppm [85] or 50 ppm [86]. Cu could be extracted from them and transported to the surface, not only by magmatic fluids but also through metamorphic fluids and meteoritic water along the faults. The great volume of the basic–ultrabasic rocks below the rifts or troughs supplies a big volume of Cu for sedimentary-hosted deposits.

A similar situation exists in the Kodar–Udokan area, confirmed by the geophysical data. The processing of gravimetric data and the 3D model of the area built on their basis [9] indicate that the high-density rocks are traced to a depth of 20 km, forming an extensive horizontal chamber. It is formed by rocks of basic composition, with a high probability. In this model, the Chineysky and Luktursky anorthosite–gabbronorite massifs represent the upper parts of the high-density columns (Figure 13). Crystallization of primary magmas led to the formation of sulfide ores within the massifs while the associated residual melt-fluids (together with meteoric waters?) could have formed the veins observed at the Prvoingamakitsky deposit. Hot magma could involve in the circulation deep and near-surface fluids, which carried copper (and partly sulfur?) from the basic rocks. Subsequently, these mineralized fluids could penetrate the pores of the sandstone and surface water, forming sulfides. In the latter case, the important role of thiosulfate bacteria in ore formation cannot be excluded.

Geochemical data for granulites, metabasites, and ultramafic rocks of the southern Siberian Platform [87,88] suggest the existence of a (sub)lithospheric source here for a long time. It was shown [89] that initially (2.7–2.9 Ga), this substrate was enriched with a mafic component with a lower Sm/Nd ratio and was isolated from the convecting mantle with Sm/Nd ≈ 0.350 for 2 billion years. Both the rocks of the Palaeoproterozoic Chinesky gabbro pluton and the Dovyrensky massif belong to the line of neodymium isotopic evolution or are closely related to the Neoarchean protolith. This substrate possessed the geochemical signature of a supra-subduction mantle that supplied magmatic material for the crustal extension of the Siberian craton at the Meso- and Neoarchean boundary. Differences in the time of reactivation of this ancient mantle and its melting are manifested in different degrees of isotopic anomalies of igneous rocks for the time of their crystallization. This substrate could be the Cu and S sources before the Chineysky and Luktursky magmas crystallized. The fluids that originated from the crystalline basement could have migrated through the fault upward into the higher structural levels where they caused ore deposition. This model was suggested by Baatartsogt et al. for the Schwarzwald district, Germany [90].

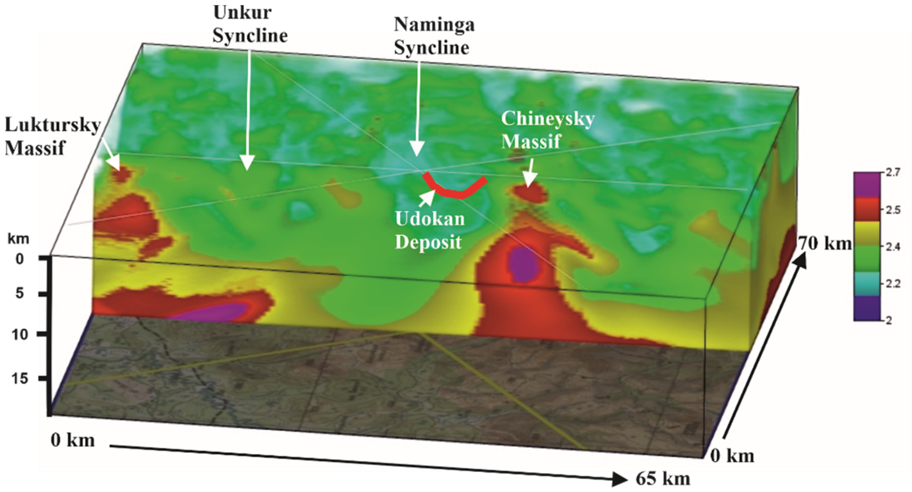


Figure 13. Cross section of gravity mass distribution across the Luktursky and Chineysky massifs and the Unkur and Naminga synclines with cupriferous sandstone deposits (Unkur and Udokan). Data for gravity field are given in arbitrary scale (after [21]).

6. Conclusions

1. Significant variations in the mineral composition of the deposits located at the different levels of the sedimentary sequence of the Udokansky complex were established: from the Krasny deposit, characterized by a diverse composition of ores with minerals atypical of Cu sandstone-hosted deposits (pentlandite, pyrrhotite, and tennantite–tetrahedrite series) to the Udokan deposit, where a chalcocite–bornite association sharply dominates.
2. The study of the sulfur isotope composition of sulfides from the deposits in the Kodar–Udokan region revealed a significant range of $\delta^{34}S$ variations in each of them (up to 40‰). Analysis of the sulfur distribution in the studied deposits shows a tendency for $\delta^{34}S$ reduction from positive values (the Krasny deposit) to strongly negative ones at the Udokan deposit located at the uppermost level of the stratigraphic sequence.

The revealed regularities can be explained not only by the probable influence of the nearby gabbro massifs (Luktursky and Chineysky) but also by the remoteness from the deep source of the ore components, i.e., the igneous rocks of the basement of the Kodar–Udokan trough.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min14030228/s1, Figure S1: Diagram Cu vs. Ag for sulfide ores at the Burpala deposit; Figure S2: Disseminated chalcocite-bornite ore at the Udokan deposit; Table S1: Composition of ore minerals, wt.%.; Table S2: Sulfur isotope data of ore minerals and ores at the deposits of the Kodar-Udokan region.

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