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Mineralogy and prospect of noble metals of gold-bearing ore breccias from ore fields of polymetallic deposits of Ore Altai

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Abstract. The object of the present study are the ore-bearing breccias of the worked-out lower-middle Devonian gold-silver barite-polymetallic Zmeinogorsky deposit belonging to the cognominal ore district and the conserved massive sulfide Chekmar deposit belonging to the Leninogorsk ore district. Both ore districts occupy an adjacent position within the northeastern depression zone of the Ore Altai megatrough. A brief structural and geological description of near-fault ore-bearing breccias, which developed within the peripheral parts of the deposits, is given. Analysis of petrographic composition of breccia fragments and their cementing material allowed to define barite-quartzite breccias of the Zmeinogorsky deposit and pyritized adularia-quartz metasomatites formed upon acidic igneous rocks and greenschists of the Chekmar deposit. Results of mineralogical studies with use of raster electron microscope show that there are ore minerals microinclusions in the detrital material and cement of breccias. Barite-quartzite breccias of Zmeinogorsk deposit contain barite, galena, Hg and Sb containing polymineral formations, tetrahedrite-boulangerite, bromargyrite, leucoxene. Microquartzites of these breccias mostly consist of quartz. Chekmar deposit ore breccias detrital material contains pyrite, barite, arsenopyrite, galena, sphalerite, zircon, titanite, leucoxene and REE minerals. Quartzitic compound of these breccias is cryptocrystalline and consists of quartz and adularia with admixtures of sericite and pyrite. Due to results obtained by use of SEM it was stated that barite, sulfides and sulfosalts of breccias contain noticeable amounts of dissipated Au, Pd, Pt, Ir. ICP-MS results confirm that studied ore breccias contain such noble metals as Au, Ag, Pd, Pt. Moreover, noble metals contents in Zmeinogorsk deposit breccias reach industrial standards while noble metals of Chekmar deposit ores can be extracted along with the processing of basic massive sulfide ores. Further study of ore breccias is important as these breccias can be considered as a noble metals containing subformation among polymetallic ores of Ore Altai.

1. Introduction

Laboratory of Structural Geology and Tectonics at the Geology and Geography Faculty of Tomsk State University has been developing the topic "Geology, minerals and issues of noble metal content of ore formations of Rudny Altai" for over 15 years [1]-[2]. Within the framework of this topic, geological and natural tectonic positions and structures of ore fields are considered [3]-[8]. At the present level studied the mineral and geochemical compositions of ore and near-ore metasomatites are studied, issues of their noble metal content and prospects for complex processing.

The methodology of studying the Ore-Altai objects was applied to the study of ore-bearing breccias, which can represent their own subformational subtype of the noble ore of Ore Altai.

The aim of the work is to study the ore-bearing breccias of two deposits of Rudny Altai, confined to the flank parts of the ore fields of deposits, the establishment of the formational type of their hydrothermal-metasomatic formations by means of geological, petrographic, mineralogical and geochemical research. Clarification of the role of tectonic processes during the formation of breccias and polymetallic ores, assessment of their potential noble metal content. Analytical studies were conducted at the Centre of Collective Usage "Analytical Center of Natural Systems Geochemistry", TSU.

Relevance of research. Ore Altai is important for the development of South Siberia and East Kazakhstan. Here the richest deposits of polymetals, gold, rare and rare-metal elements have been known for a long time. Industrial development of the area began with direction of Peter the Great and continues to this day. Ore Altai is an important mineral resource base of non-ferrous and noble metals for Russia and the main one base for Kazakhstan. On the territory of Ore Altai over a thousand ore objects are known, including over 70 industrial ones.

2. General description of ore bearing breccias

The actual material. The tectonic gold-bearing barite-quartzite breccias of the Zmeinogorsky deposit have been surveyed by the staff of the Research Laboratory of Structural Geology and Tectonics several times over the past 15 years with the selection of rock material for research. Ore breccias of the Chekmar deposit were studied by A.S. Semiryakov by the course of prospecting works in 2016-2017, as part of the Geological Prospecting Service for East Kazakhstan, Kazzinc LLP. He selected a number of samples of the host rocks of the Uspen Formation, near-ore metasomatites and ore breccias of the preserved Chekmar deposit of the Guslyakovsky ore field of the Leninogorsk ore district.

In relation to the studied ore-bearing breccias, the following information deserves attention. The largest in its time Zmeinogorsky mine began its work in 1736 and by the early 20th century the reserves of rich barite-polymetallic gold-silver ores were depleted. Nevertheless, in 1905, the Imperial Cabinet of the Russian Empire and Austrian subjects Prince Alexander Thurn und Taxis and Doctor of Law Joseph Janne renegotiated a lease for the mining industry in certain areas of the Altai district. This agreement gave tenants the right "to explore and develop gold, silver, lead, zinc and other metals and minerals along with them ..." [9]. The main subject of interest of shareholders at Zmeinogorsky mine were the so-called gold-bearing quartzites.

For the years 1905–1912, the Austrian concessionaires obtained a total of 533.57 kg gold and 277.08 kg of silver at Zmeinogorsky mine [10]. In the year when World War I began, Austria ceased its operations in Altai. The Zmeinogorsky agreement was officially handed over to the English joint stock company Russian Mining Corporation, for which it was of particular interest that ore objects of the Zmeinogorsky type with gold-bearing quartzites, which, possessing large reserves even with low contents of precious metals, could become the basis for organizing large-scale gold mining. The Russian Mining Corporation produced 33,538 tons of ore, from which 167.44 kg of gold and 258.27 kg of silver were produced. As a result, this type of gold ore was completely exhausted, and the nature of quartzite has not been reliably established.

According to a number of characteristics, the quartz-like component of the ore breccias of the Chekmar deposit, Leninogorsk ore district, has features similar to those of the Zmeinogorsky deposit. This fact and the large-scale development of ore breccias served as the basis for their detailed study in order to ascertain their potential gold bearing and formational affiliation.

2.1. The Barite-Polymetallic Zmeinogorsky deposit

Gold-bearing barite-quartzite breccias of the Zmeinogorsky deposit are confined to the southern flank of the spent barite-polymetallic gold-silver deposit. This flank is made up of a massively layered clayey limestone block of the Ems nizhnemelnichnaya formation, thrown up along the system of sublatitudinal faults. The rocks have previously experienced layer-by-layer selective silicification under the action of a series of inculcated sub-concordant of the early Devonian rhyolite-dacite sills, established by drilling. In the course of the tectonic movements during the pre-ore and syn-ore stage, the raised block experienced crushing and fracturing, and then “cementation” by the infiltrated barite material, eventually becoming a rather large near-fault stock-vein zone.

An essential part of gold-bearing breccias is different-sized fragments (from 5–10 cm to 40–50 cm in diameter) of chalcedonic bluish-gray quartzites penetrated by filamentous barite veins of very different thickness (figure 1).

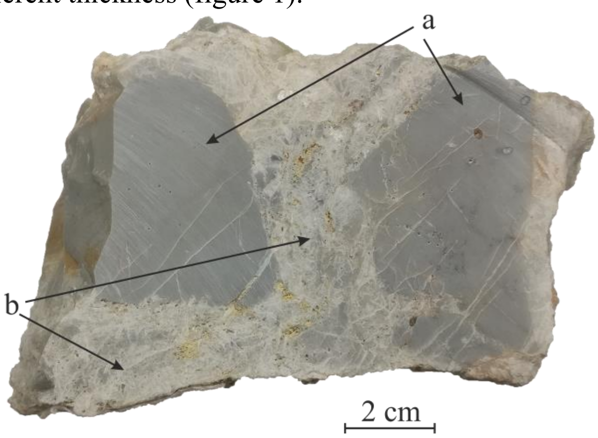

Figure 1. The barite-quartz breccia of stockwork zone of the Zmeinogorsky deposit: a — fractured quartzite pieces; b — veinlets of barite different thickness, cementing a quartzite.

2.2. The Volcanogenic Massive Sulphide Chekmar deposit

The Chekmar deposit was discovered in 1976 and was actively studied by scientists and production organizations. In the published literature of the 80s, the geological model of the deposit was described; however, the main focus of research was on the characteristics of industrial mineralization and the conditions of localization of ore bodies. The structure of the field also includes crushing zones, which are given only a superficial description [11]-[13]. Ore breccias were not specifically studied, the nature of their metasomatic transformations has not been established, they were identified as quartzites, which, as shown by our research, belong to the quartz-adular type. Against the background of massive pyrite-polymetallic ores, the pyrite mineralization of breccias, apparently, was simply neglected, especially since no one regarded these formations as an independent industrial type of ore. This work represents the one of first attempt to comprehensively study the ore breccias of the Chekmar deposit, which until now had been considered as secondary quartzites without determining their nature and formation.

The term "ore breccias" of the Chekmar deposit refers to tectono-hydrothermal breccias of a quartz-adducer composition with manifestation of significant (5–10%) pyrite mineralization with accessory inclusions of zircon, sphene, leucoxen, galena, sphalerite, and others. processing in the conditions of the moving environment of the Northeast zone of the crushing, manifested in the formation of several generations of pyrite, a complete metasomatic transformation of the original rocks and intense superimposed cracks of fragile nature (figure 2).

The described ore breccias are developed on the southwestern flank of the Chekmar deposit and are confined to local crushing zones. The studied samples were selected at the contact of the upper pack of the Assumption suite (D_2ef-žv_1) with the ore body of lead-zinc composition. Along the crushing zones, intense silicification and adularization are noted.

The basis of ore breccias is composed of fragments of relict rocks, the primary composition of which can only be reliably established quite conditionally due to the almost complete loss of the primary structural and textural characteristics and replacement of the quartz-potassium-sparred fine-grained aggregate (quartz-adularar aggregate). Visually, this rock looks like a cryptocrystalline siliceous rock. It is very difficult to detect the presence of a CBS on a polarizing microscope, but it is not possible to macroscopically.

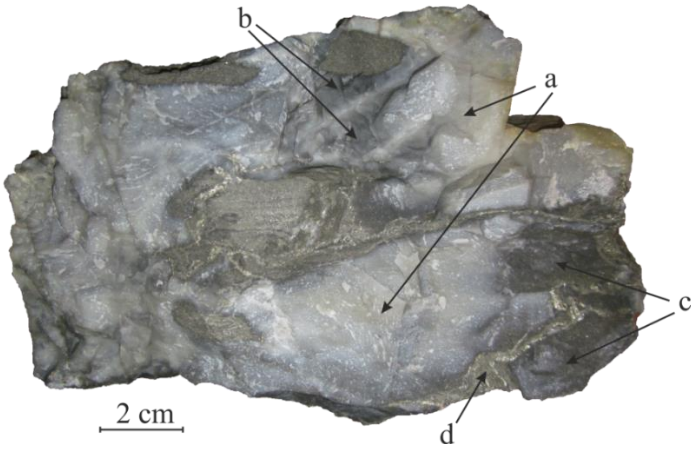

Figure 2. Sample of ore breccia, selected on the flank of the Chekmar deposit: a — light colored tectonitized and metasomatized fragments of primary acidic rocks; b — the marginal part of the primary fragments, saturated with fine-grained pyrite; c — dark-colored areas of transformed quartz-chlorite-sericite schists; d — quartz-pyrite veinlets.

The color of quartz-adulare rock is light gray to whitish. The penetration of ore matter into the depth of such debris occurs only a small distance from their outer borders, which gives the metasomatic rock gray, sometimes dark gray color.

In general, two types of primary rocks are established, transformed in accordance with tectonic processes and metasomatism in ore breccias:

- volcanic rocks of acidic composition and secondary quartzites formed from them (figure 2, a), having light gray color on the periphery of fragments (figure 2, b);
- metaslants with the original, apparently, quartz-chlorite-sericite composition (figure 2, c).

3. Mineralogy of Ore Breccias

This section provides information on the mineralogical composition of the breccias of the Zmeinogorsky barite-polymetallic deposit and the volcanogenic massive sulphide Chekmar deposit. Studies of the mineral composition of breccias, in addition to macroscopic studies on a polarizing microscope, were carried out by scanning electron microscopy and X-ray microanalysis on a microprobe.

3.1. The mineralogy of the breccias of Zmeinogorsky deposit

The mineralogy of the near-ore metasomatites was studied in detail by K.V. Bestemyanova, the results of the work are set out in the publications [14]-[16]. The barite-quartzite breccias of the Zmeinogorsky deposit, when they were studied on a raster electron microscope, revealed the mineralogical composition, which briefly describe in this subsection

3.1.1. A fragments of quartzite. Quartzite fragments have almost pure quartz composition (wt.%): Si 46.74, O 53.26 with an insignificant proportion (0.2-0.4%) of aluminum. The texture of quartzite is cryptocrystalline, structure is homogeneous. Barite, bromargyrite, galena, tetrahedron-like sulfosols and polymineral formations based on mercury and antimony are established in the form of small rare inclusions in quartzites. Rutile and leucoxene are also installed.

Barite forms single grains and less often their accumulations. The size of the grains ranges from several microns to 20-30 microns. By microprobe are set Au and Pt as a constant impurity.

Bromargirite forms inclusions similar to barite, but of a more complex structure such as emulsion-shaped two-three-phase mineral formations with sizes up to 20 microns (figure 3). The composition of bromargyrite is very unstable, the average composition is as follows (wt.%): Ag 74.17, Br 18.08, Cl 2.88, J 4.55, Fe 0.32.

Galenite is contained in the form of tiny grains of 5–15 µm in size, immersed in a uniform cryptocrystalline quartzite matrix. Galena contains elevated levels of Au and PGMs.

Polymineral formations based on mercury and antimony are observed in the form of group clusters of complex structure. Their composition is as follows (wt.%): Hg 48.93, Sb 1.21, Ag 5.36, Br 8.86, Cl 6.38. Other analysis: Sb 30.51, Fe 16.97, Br 8.86, Pb 8.80, Ag 4.31, As 1.32, Cu 0.51, Cl 1.25. The size of the formations and their clusters from a few microns to 20–40 microns.

Leucoxene (rutile) forms rare single grains or sparse clusters of up to 40 microns in size across. Individual grains have regular rectangular outlines of peppered cuts. Composition (wt.%): Ti 59.62, O 39.98.

3.1.2. A barite of vein breccias. Barite vein breccias has an almost monomineral composition, with the exception of micro-formations of simple and complex mineral composition, like formations in quartzite. Here besides the barite itself are established: bromargyrite, galena, tetrahedrite.

Barite forms a fine-medium-grain aggregate of grains, transitioned more large-crystalline well-formed crystals with elongation sizes up to 3–7 cm. The average composition of barite (wt.%) Ba 56.24, Sr 0.82, S 14.51, O 28.43. By microprobe are set Au and Pt as a constant impurity.

Galena forms fine grains of uniform structure, 3–7 microns in size. It contains a constant admixture of Au and platinoids.

Bromargiritis is noted in the form of rare small grains of heterogeneous composition and structure with sizes up to 40–50 microns. The composition of bromargyrite in barite veins corresponds to the composition of its inclusions in quartzite.

Tetrahedrite forms aggregate polymeineral accumulations (mineral intergrowths) of sulfosalts and, probably, galena, based on Pb and Sb. Sizes of inclusions from 5 to 20 microns. Significant Au and Pt contents are noted by microprobe in these formations.

3.2. The mineralogy of the breccias of Chekmar deposit

For ore breccias of the deposit Chekmar the following mineral composition of rock-forming minerals is established.

Quartz and KPS (orthoclase) form a solid cryptocrystalline aggregate in ore breccia samples. There are marked areas of significant distribution of the quartz aggregate, areas of predominance of KPS, as well as their joint distribution (figure 4).

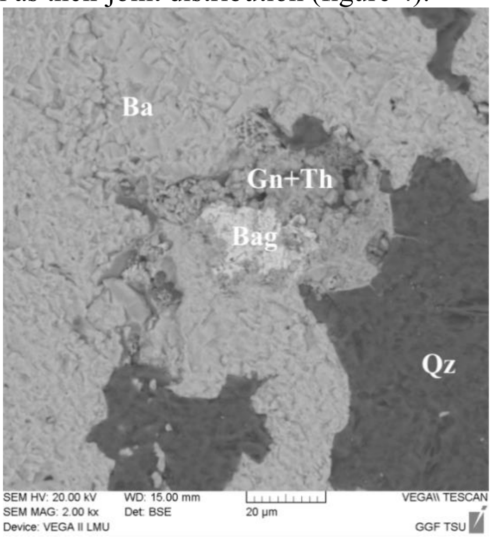

Figure 3. Isomorf mineral formation of bromargyrite (Bag) and polymeineral accumulations of galena (Gn) and tetrahedrite (Th) in the barite vein aggregate (Ba) among fragments of quartzite (Qz), Zmeinogorsky deposit. The pictures were taken on a raster electron microscope in BSE mode.

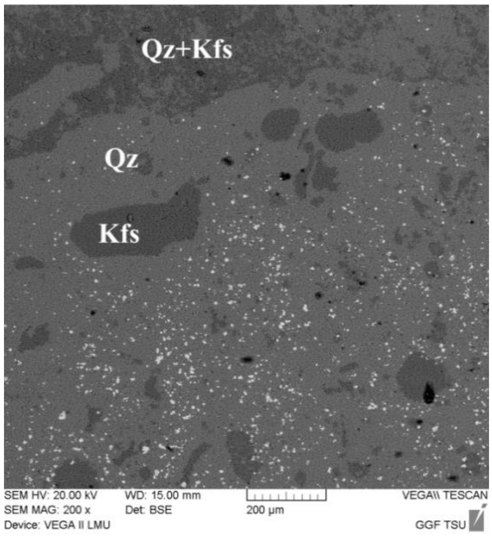

Figure 4. Cryptocrystalline microstructure of substantially of quartz (Qz), substantially of addural (Kfs), bimineral quartz-adular (Qz + Kfs) aggregates, light coloured grains - finely scattered pyrite, Chekmar deposit. The pictures were taken on a raster electron microscope in BSE mode.

Sericite is sparsely distributed and encrusts fine- and medium-grained pyrite grains.

The small quanties contains barite, which is characterized by a single development of grains inside the quartz-adular aggregate, as well as performing small cracks in the pyrite grains. Barite secretions are largely xenomorphic.

Typical accessory minerals — zircon and sphene are very limited. However, zircon grains have significant geochemical differences among themselves, which allow them to be assigned to different geochemical groups (possibly generations). Leucoxen, as a product of decomposition of sphene, is also developed limited. The grains of the latter have uneven outlines.

In the course of research, grains of a rare earth mineral were found in the sample with the chemical composition most closely related to euxenite. The crystals are imperfect, xenomorphic. To establish the exact mineral species, additional research is required. This find has mineralogical interest.

Sulphides and sulfosalts are occurring:

Arsenopyrite is represented by very rare well-formed grains. In the chemical composition of arsenopyrite in a latent form contains an admixture of Au and PGM.

Galenite occurs very rarely, mostly with small inclusions or performing microcracks in pyrite grains. This indicates at least two of its generations. The galena also contains Au and PGM. The sphalerite is more rarely spread and it is association with galena.

Pyrite composes a significant portion of breccia and is characterized by several of forms of aggregate — at least three generations of pyrite are reliably established:

1. The first generation of pyrite is characterized by fine-grained interspersed grains with a size of less than 0.05 mm. Distributed within quartz-adular metasomatites unevenly and gives them a light gray tint.
2. The second generation of pyrite is represented by fine-medium-grained grains, and composes separate aggregates of jagged and banded texture. The aggregates of this generation of pyrite are enclosed in quartz-adular metasomatic formations and are also superimposed with respect to them.
3. The latest is the third - veined pyrite generation. The abundance of veins and veinlets that are multi-oriented and often intersecting each other, suggests that subsequent processes of crushing breccias and healing veins with quartz-pyrite solution have manifested themselves more than once.

However, it is impossible to speak unequivocally about the exact number of generations of pyrite, rather, we are talking about the most characteristic forms of manifestation of pyrite mineralization.

Based on the mineral composition of breccias and the enrichment of their lithophilic elements, it can be concluded that there is a genetic relationship with metasomatites with acidic intrusive rocks that are widely distributed within the ore field.

4. Prospect of mining noble metals

The determination of the geochemical composition and concentrations of noble metals of the ore breccias of two deposits was carried out by the ICP-MS method using methods MMP 001-CMS-2007 "Methods for measuring the mass fractions of elements in rocks by the method of mass spectrometry with inductively coupled plasma".

It analyzed samples of ore-bearing breccias of both deposits (table 1).

Zmeinogorsky deposit:

1) Zm.1 — a piece of quartzite;
2) Zm.2 — gross breccia of barite-quartzite composition;
3) Zm.3 — barite vein, "cementing" debris.

Chekmar deposit:

1) Ch.1 — empty quartz-adular light colored metasomatite;
2) Ch.2 — fine-grained and fine-grained massive pyrite rock;
3) Ch.3 — breed with gangue fine- and medium-grained pyrite;
4) Ch.4 — sprayed pyrite rock;
5) Ch.5 — dark gray rock with massive pyrite mist.

Table 1. Content of noble metals in ore breccias of the Chekmar deposit and barite-quartzitic rocks of the Zmeinogorsky deposit according to ICP-MS, ppm.

Element	Ch.1	Ch.2	Ch.3	Ch.4	Ch.5	Zm.1	Zm.2	Zm.3	Clarks in the Earth's crust *
Ru	0.02	0.02	0.02	0.02	0.02	0.002	0.007	0.006	$4\cdot10^{-3}$
Pd	0.41	0.26	0.35	0.31	0.34	0.328	1.051	0.893	$9\cdot10^{-3}$
Ag	0.58	4.81	5.35	5.28	1.12	58.793	491.422	885.699	0,073
Pt	0.06	0.03	0.04	0.03	0.05	0.010	0.007	0.003	$5{,}7\cdot10^{-3}$
Au	0.03	0.10	0.17	0.15	0.00	0.504	5.336	19.276	$3{,}5\cdot10^{-3}$

* Note: Clarks of elements in the Earth's crust is taken according to L.N. Ovchinnikov [17].

For ore breccia of Chekmar is characterized by an elevated to significant content of precious metals, which exceed the clarks ones, but do not reach industrial values. Pyrite, by virtue of its quantitative content, is the main carrier of the noble metal mineralization of this type of breccia fringing the massive sulfide Chekmar deposit. Pyrite in samples is unevenly distributed and, on average, its content ranges from 5 to 10–15%, which does not provide industrially significant concentrations of noble metals in ore breccias. But in the case of increased pyrite content of — 30–50%, ore breccias can be of industrial importance.

According to ICP-MS data, quartzites, vein barite and gross sample of barite-quartz breccias of the Zmeinogorsky deposit, like as breccias of the Chekmar deposit, are specialized in Pd, Ag and Au, but with the difference that Au and Pd content in them reach industrial concentrations (Au 5.3–19.28 ppm; Pd 0.89–1.05 ppm). At the same time, the Pt and Ru contents are also one or two orders higher than the clarks ones.

In general, when analyzing the geochemical data of ICP-MS, the ore-bearing breccias of both deposits have both dominant common and distinctive features. Among the common features are their specifications for noble metals, the contents of Ti, V, Cr, Mn, Co, Ni reduced relative to the clarks of the earth's crust, and Li, Be, Sc. At the level of clarks and below, ore breccias contain REE, as well as elements such as Ga, Sr, Rb, Nb, Ba, Pb, U, Th, Mo Sb, Te are at the level and significantly higher than the clarks. The results of the analytical research are presented in the statement of the results of analytical studies in the publication [18].

5. Main conclusions

The studied mineralized breccias of two deposits belonging to adjacent ore areas of the Ore Altai megaprogib indicate that the tectonic factor played an essential role in the formation of both the Lower-Middle-Devonian Zmeinogorsky deposit and the Middle-Upper Devonian Chekmar deposit. Faults accompanied by zones of fracturing and crushing promoted the circulation of ore-bearing solutions and the formation of near-ore metasomatites and the ores themselves in the form of ore pillars, stockworks, lenses, and in favorable conditions of sublayer bodies, in layered strata.

The main minerals concentrators of noble metals in the studied ore breccias are barite, sulfides, sulfosalt and its own noble metal mineralization. In general, hidden (scattered) noble metal mineralization dominates here.

The total mass of mineralized near-fault metasomatites, including ore breccias, within the ore fields of deposits are very significant, often exceeding the volume of ore bodies. At significant and industrial concentrations of noble metals in them, such as, for example, in barite-quartzite breccias of the Zmeinogrsky deposit, they should be regarded as a subtype or subformation of the ores of the main deposit. The ore breccias of the Chekmar type may be of interest when mining the main ores of the deposit. Their study and accounting will significantly increase the reserves of precious metal raw materials of the treasury of Ore Altai and the whole of Southern Siberia.

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