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Barite-polymetallic mineralization of Zmeinogorsk ore district and some genetic aspects of its formation

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Abstract. Zmeinogorsky ore district is located in the northwest part of Ore Altai megatrough, which has long-lasting history of its development and complicated geological structure. Within the ore district, which is the northwest part of the devonian Zmeinogorsk-Bystrushinsky trough, ore mineralization is associated with the system of northwest border faults and cross branch faults.

There were four main stages and five phases of minerogenesis. The first stage is the stage of oregenesis beginning and quartz-chlorite-sericite wall-rock alteration rocks formation. Ore deposition and intense tectonics took place during the second stage. The third stage is the most longstanding and productive ore formation stage. There are five distinct minerogenesis phases within this stage. The fourth stage expressed in erosion development and supergene alteration of already formed ore bodies with oxidation zone formation.

Main ore minerals are pyrite, chalcopyrite, sphalerite and galena. Minor minerals are tetrahedrite, bornite, tennantite and chalcocite. Precious metals minerals are acanthite, gold, electrum, gold and silver amalgams. Barren minerals are barite, quartz, calcite, gypsum.

According to obtained data average isotopic composition of third stage sulphides is: pyrite -0,2‰, chalcopyrite 0‰, galena +0,5‰, sphalerite -1,2‰ for the first complex; chalcopyrite -1,9‰, galena -3,4‰, sphalerite -2,3‰, tetrahedrite -3,7‰ for the second complex; tennantite -12,8‰, bornite -8,9‰ for the third complex. Sulfur isotopic composition variations indicate source inhomogeneity. Thus, there was dominant source change from mantle one in the beginning to crustal one in the end.

Main oregenesis stages took place in the range of temperatures between 170 and 210°C and in the mineral-forming solutions salinity range between 3 and 10 wt % NaCl equiv.

1. Introduction

Zmeinogorsky ore district is the part of Ore Altai polymetallic belt, which is one of the world's largest provinces with polymetallic deposits and lead and zinc ores reserves. There are two subformations (pyrite-polymetallic and barite-polymetallic) deposits belonging to Zmeinogorsky ore district [1]. Different type deposits formed in different geological conditions (even within the same subformation) and have mineral composition differences.

Barite-polymetallic subformation deposits bear five minable components: Cu, Pb, Zn, Au and Ag. This determines the necessity of barite-polymetallic deposits structural features and mineral composition study especially while these deposits are under dynamic production, mineral resources base is depleting and new objects finding is essential.

Barite-polymetallic subformation ores geological position, mineral composition features and genesis aspects was reviewed by the examples of three main Zmeinogorsky ore district deposits: Zmeinogorskoe, Zarechenskoe and Strizhkovskoe, which are located in the northwest part of the district.

Ore bodies contain a few different types of ores, which replace each other in the following sequence (from bottom to top): pyrite-polymetallic (among which it is possible to distinct essentially copper ones allocated within lower Paleozoic strata predominantly); polymetallic (among which it is possible to distinct essentially zinc, essentially lead or lead-zinc ones); barite-polymetallic (among which it is possible to distinct essentially barite ones). There are 45 different minerals, among which

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there are sulfides, sulfosalts, tellurides, oxides, oxygen acids salts, native elements and intermetallic compounds, making up the ores composition [2, 3].

2. Geological position of deposits

Zmeinogorsky ore district is the part of Ore Altai megatrough (figure 1), which belongs to Hercynian Ob-Zaysan collision area. The trough occupies boundary position between Kalba-Narym zone of Ob-Zaysan area at the southwest and Caledonian Altai at the east. Besides main structure-forming longitudianl regional faults with northwest strike there is a number of submeridional faults and a combination of faults with northeast and sublatitudinal strike [4].

Zmeinogorsky ore district is located in the north part of Zmeinogorsk-Bystrushinsky volcanogenicterrigenous trough, which is the northern part of northeast megatrough boundary depression zone.

There are two structural levels – caledonian and hercynian – in the structure of Zmeinogorsk-Bystrushinsky trough and its ore deposits [5]. At that caledonian structural level consists of korbalikhinskaya suite dynamometamorphites while hercynian structural level consists of volcanogenic and volcanogenic-terrigenous lower, middle and upper devonian sediments of melnichnaya (D_{1-2} mn), sosnovskaya (D_{2} ss), zavodskaya ($D_{2}zv$) and kamenevskaya (D_{2-3} kmn) suites.



Figure. 1. Ore Altai megatrough. 1 – Devonian and predevonian zmeinogorsky complex granitoids, 2 – Carboniferous aleysky complex granitoids, 3 – early Permian kalbinsky complex granitoids, 4 – unsubdivided mafic intrusions (D, C, P), 5 – metamorphic complexes (O-S), 6 – unsubdivided strata, 7 – boundary depression zones strata a) middle and upper Devonian and b) lower, middle and upper Devonian bystrushinsky and beloubinsky synclinorium strata, 9 – upper Devonian and lower Carboniferous Kalba-Narym zone strata, 10 – Altai Baikalides and Caledonides, 11 – Kalba-Narym zone, 12 – Barnaul sag, 13 – dynamometamorphic rocks of basement highs (R- \mathcal{C}_1), 14 – first-order suture zones, 15 – disjunctive faults, 16 – structural-compositional complexes boundaries.

During the study it was stated that Zmeinogorsky district ore areas are located within small-scale early-middle Devonian ring-swell volcanic morphostructures. Horst-like highs of greenschist

metamorphites, overlying early-middle Devonian volganogenic-terrigenous rocks and penetrating Devonian plutonic and subvolcanic bodies (e.g. dikes) take part in these morphostructures composition. Ore-bearing rocks are early Devonian in general.

Main ore-bearing strata mostly are Emsian rocks of nizhnemelnichnaya subsuite where impregnated, stringer-impregnated, less often – massive ores concentrate in the lower terrigenous sedimentary stratum (argillites and aleurolites predominantly, limestones and sandstones less frequently with small tuffs layers); most part of massive ores is concentrated within bedding-plane and cross bodies at crystal tuffs horizons and terrigenous-carbonate stratum [6, 7].

Oregenesis took place during active tectonics with repeated changes from compression and to tension conditions and proper ore areas morphostructures formation. Vein-like and lens-like ore bodies are assigned to disjunctive faults, clastation and schistosity zones, cleavage and separation cracks; at that ore textures are breccia, stringer-impregnated, impregnated, massive and inequigranular ones, so structural and tectonic conditions predominate in barite-polymetallic ores distribution control. In auspicious environment when ores are forming layer by layer lithologic-stratigraphic conditions influence significantly too.

3. Methods

Data on ore and barren minerals composition and pictures of mineral associations and individuals interrelations in back-scattered electrons (BSE) mode was obtained by carrying out the electron microprobe analysis with use of scanning electron microscope Tescan Vega II LMU, which is equipped with energy-dispersive spectrometer (with Si(Li) Standart detector) INCA Energy 350.

Microelement composition was studied by inductively coupled plasma mass spectrometry (ICP–MS) with use of Agilent 7500 x spectrometer. These analyses were carried out at the collective use center «Analytic Center of Natural Systems Geochemistry» of Tomsk State University (Russia). Au and Ag contents determination was carried out by atomic absorption spectroscopy. Thermo- and cryometry of fluid inclusions were conducted with use of Linkam equipment. This analysis was carried out at the Analytical Center of multielement and isotopic research of Sobolev's Institute of Geology and Mineralogy SB RAS (Russia).

Variations of stable sulfur isotopes contents were studied at the stable isotopes laboratory of Far East Geological Institute of FEB RAS.

4. Results and discussion

There was multidtage and multiphase oregenesis at the studied objects. There are a number of mineral complexes related to four main stages and five steps [8].

During the premineral stage (the first one) wall-rock alternation (quartz-sericite, quartz-chlorite and quartz-chlorite-sericite metsomatic rocks formation) took place. Studied metasomatic rocks are early Devonian altered ones, which formed due to carbon dioxide solutions impact on poorly lithified early Devonian volcanogenic-sedimentary host rocks. Zones of their distribution are related to sublatitudinal and submeridional disjunctive faults and schistosity zones. Studied rocks have indistinct zoning: the inner part of metasomatic aureole is filled by quartz-sericite rocks while the peripheral quartz-chlorite-sericite and quartz-chlorite rocks. Mineral paragenesis of these rocks is rather plain: major minerals are quartz, chlorite, sericite and pyrite, minor ones are zircon, apatite, rutile, accessory ones are chalcopyrite, galena, sphalerite, barite, monazite and xenotime [9].

According to obtained data pyrite sulfur isotopic values in these rocks vary from -0.9% to +1.6%. This indicates that there was juvenile sulfur source.

According to results of study of precious metals contents there are low gold and silver contents in altered rocks. Thus, in quartz-sericite rocks Au contents vary in 0,02–0,10 ppm range; Ag contents vary in 1,0–2,5 ppm range; in quartz-chlorite-sericite rocks there are 0,12–0,38 ppm Au contents, 0,49–2,1 ppm Ag contents; in quartz-chlorite ones there are 0,018–0,12 ppm Au contents, 0,49–0,68 ppm Ag contents. Apparently gold and silver are scattered in sulfides.

Pyrite, sphalerite, chalcopyrite and galena deposition began during the second stage. This stage took place in the end of Emsian age and the beginning of Eifelian age (D_1) and was short-time apparently. None the less intense tectonics took place. Textures are breccia and impregnated ones, structures are crush and replacement (second stage sulfides are replaced by third stage sulfides usually) ones. This stage ores make up no more than 10-15 % of ores total volume (figure 2).

The third stage of oregenesis was the most long-lasting and productive one. About 80 % of ores deposited during this stage. Syn- and postmineral tectonics and faults and jointing zones activation took place during this stage.

The first complex of the third stage includes chalcopyrite, sphalerite, galena and less often pyrite. Following textures are typical for the third stage: impregnated, stringer-impregnated, stringer and massive ones; typical structures are inequigranular, fine-, medium- and coarse-grained, emulsion, colloform, corrosion, clastic, contortion, less often replacement ones.

The second complex of the third stage includes barite, sphalerite, galena, chalcopyrite, tetrahedrite, arsenopyrite, acanthite and quartz. Barite fluid inclusions homogenization temperature varies in 190-210 °C range, salinity is 6,0-10,0 wt % NaCl equiv.

Quartz fluid inclusions homogenization temperature varies in 170-190 °C range, salinity is 3,0-4,5 wt % NaCl equiv.

The third complex of the third stage includes bornite, tennantite, chalcocite, less often - galena, chalcopyrite and barite. Minerals of this complex fill the stringers and small (up to 2 cm size) nests. There are higher gold contents (up to 60 ppm) in this complex than in the other ones.

The fourth complex of the third stage includes barren minerals mostly: there are quartz, biotite, barite, calcite, hematite and gypsum. These minerals fill the fissures, stringers and dissolution cavities.

Average chemical compositions of main sulfides included in distinguished complexes and average sulfur isotopic compositions are presented in table 1.

	-			-	-		-					Central
Minerals					Elen	nent, wt	. %					cases of
						<i>,</i>						δ34CDT,
												% 0
	S	Fe	Cu	Zn	As	Se	Ag	Cd	Sb	Pb	sum	
				Sulfid	es of the	first (I) comple	ex				
Pyrite	52.8	46.8	-	-	-	-	-	-	-	-	99.6	-0.2‰
Chalcopyrite	34.26	29.7	35.1	-	-	-	-	-	-	-	99.06	0‰
Sphalerite	35.02	-	-	64.96	-	-	-	-	-	-	99.98	-1.2‰
Galena	13.86	-	-	-	-	-	-	-	-	86.06	99.92	+0.5%
				Sulfides	of the se	econd (II) comp	olex				
Chalcopyrite	34.81	31.12	33.78	-	-	-	-	-	-	-	99.71	-1.9‰
Sphalerite	34.27	0.29	-	64.12	-	-	-	1.2	-	-	99.96	-2.3‰
Galena	13.23	0.72	-	-	-	1.05	-	-	-	85.34	100.34	-3.4‰
Tetrahedrite	24.72	1.21	38.66	7.34	4.32	-	0-17	-	23.75	-	100	-3.7‰
				Sulfide	s of the t	hird (II	T) comp	lex				
Bornite	25.51	11.36	62.86	-	-	-	0-5	-	-	-	99.73	-8.96‰
Tennantite	30.98	0.63	40.34	7.0	15.47		0.4		5.96		100.38	-12.8‰
Chalcopyrite	35.26	30.34	34.37	-	-	-	-	-	-	-	99.7	-
Galena	13.72	-	-	-	-	-	1.43	-	-	84.17	99.32	-
Chalcocite	19.4	-	78.0	-	-	-	2.2	-	-	-	99.96	-

Table 1. Average chemical and isotopic composition of major sumues of distinguished complexe

Postmineral stage of (the fourth one) developed significantly and expressed in partial tectonic and hypergene alteration of the ore bodies with oxidation zones formation (Zmeinogorskoe and Strizhkovskoe deposits).

Besides major components (Cu, Pb, Zn) there are also (ppm): Sc (0,06-0,7), Ti (3,0-205,0), V (0,5-10,0), Cr (0,1-4,5), Co (1,2-22,0), Ni (0,3-4,7), Ga (0,5-6,0), Rb (0,5-14,0), Sr (0,1-5,0), Y (0,03-1,5), Zr (0,2-9,0), Nb (0,02-0,9), Cs (0,03-0,1) in *polymetallic* ores; Sc (0,01-0,3), Ti (5,0-41,0), V (4,5-8,0), Cr (0,1-1,8), Co (9,7-36,0), Ni (0,3-10,0), Ga (2,0-10,0), Rb (3,0-8,0), Sr (2,0-192,0), Y (0,2-1,0), Zr (0,5-3,0), Nb (0,03-0,25), Cs (0,03-0,1) in *barite-polymetallic* ores; Sc (3,5-9,0), Ti (400,0-2100,0), V (8,0-60,0), Cr (10,0-43,0), Co (3,0-25,0), Ni (11,0-32,0), Ga (2,5-12,0), Rb (0,1-0,7), Sr (5,0-11,0), Y (1,5-8,5), Zr (15,0-70,0), Nb (1,5-5,0), Cs (0,01-,015) in *early Paleozoic copper* ores.

Precious metals contents vary from 3,2 to 60 ppm for gold and from 91 to 500 ppm for silver depending on the ore type. There is precious metals (silver and gold) minerals diversity. These elements are present both in bearer minerals and concentrator minerals. Bearer minerals (sulfosalts, intermetallic compounds, native elements) are native silver, electrum, argentite (acanthite), gold and silver amalgams, stromeyerite, hessite, jalpaite. Native silver occurs at all the three deposits (in mostly polymetallic ores); there are both separate inclusions and intergrowth with argentite (acanthite) or chalcocite. There is Te admixture (0,4%) in Zarechenskoe deposit silver. Argentite (acanthite) occurs rather often. Sometimes it forms zonal structures, sometimes it forms separate inclusions and sometimes it forms a "plaque" on fahlore and chalcopyrite.

Hessite (figure 2, e) is present in mostly pyrite ores ore in polymetallic ones. Oftentimes there are also native tellurium inclusions (hessite and native tellurium are found together in galena very often). Silver amalgams are widespread in all types ores, gold amalgams are present in latter bornite-tennantite associations (this association is the most rich with electrum and gold and silver amalgams inclusions). Stromeyerite and jalpaite fill stringers in main ore minerals (chalcopyrite, sphalerite, galena) oftentimes.

Precious metals (silver mostly) concentrator minerals are tetrahedrite (here are the highest Ag contents up to 17%), tennantite, chalcocite and bornite (the lowest contents).



Figure. 2. The basic ore structures. a-brecciated ores, brecciated fragments are represented by aggregates of pyrite I (py) and sphalerite I (spl); b- structure crumpling in galena II (gn); c-emulsion structure of the decomposition of the solid solution of chalcopyrite II (chp) in sphalerite II (spl); d- zonal-ring aggregate, consisting of tetrahedrite, argentite, silver and galena; e- segregation of native tellurium, hessite, in galena; f-isolation of of native gold in fahlore grain.

5. Conclusions

Structural and tectonic position of Au-Ag barite-polymetallic ores of Zmeinogorsky ore district is determined by following circumstances: 1) Caledonian basement and transgressively overlying Devonian fault-lined and slightly plicated volcanogenic-terrigenous-sedimentary cover presence; 2) active disjunctive tectonics in subanticlinorium zone of Zmeinogorsky trough; 3) system of boundary northwest faults and their branch faults, which controlled volcanic structures location during the Devonian magmatites formation, controls ore bodies location in Zmeinogorsky ore district; 4) tectonics determine the barite-polymetallic ores distribution but in case of auspicious conditions lithologic-stratigraphical influence may also become very significant, when rising ore-bearing solutions used stratigraphic niches and became not only vertically distributed but also horizontally distributed. Oregenesis began in early Devonian period (Emsian age in particular).

According to obtained data tectonic zones were activated repeatedly and these activations were followed by simultaneous oregenesis processes, so barite-polymetallic mineralization has multistage and multiphase character (there are two main stages and 5 main phases of the oregenesis). Ores consist of five mineral complexes, which correspond to 5 phases, are same for all studied deposits and reflect pulsation of medium-low-temperature hydrothermal alteration processes. Main stage sulfides deposition took place at 170-190 $^{\circ}$ C.

According to data on sulfur isotopic composition (from 0 to-3,5‰), one can see that from initial to final stages there was sulfur source change. Thus, there were mantle source in the beginning and crustal source in the end [10]. Significantly lightweighted sulfur in the third complex sulfides (bornite and tennantite) may be considered as a result of partial oxidation in the ore-bearing solution during the oxidation potential increase when isotopes are shared between oxidative and reductive forms of sulfur, at that the latter ones become enriched with more light S^{32} isotopes.

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