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GEOCHEMISTRY

Genesis of the Berezitovoe Gold–Polymetallic Deposit: Evidence from the Isotope Composition of Lead, Oxygen, and Sulfur

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The results of the study of stable oxygen, sulfur, and lead isotopes in rocks and ores of the Berezitovoe gold–polymetallic deposit in the Upper Amur allowing us to clarify the debatable problems of its genesis are discussed in this paper. The importance of this problem is determined by the fact that the considered deposit is represented by an ore object of a fluid–explosive nature related to poorly studied and special types, which are relatively abundant in adjacent ore areas of East Transbaikalia.

The deposit is located in the northwestern part of the Amur area, within the eastern part of the Selenginо–Stanovoi Terrane (southeastern frame of the North Asian Craton), in the junction zone with the formations of the northern part of the Mongol–Okhotsk foldbelt. The deposit is represented by metasomatic sulfide-bearing tourmaline–garnet–muscovite–quartz rocks, which compose a steeply dipping body with the shape of two combined overturned cones in a massif of Paleozoic porphyric granodiorite. The ore body of the deposit has a complex lens-like shape in plan. Its length on the surface reaches 950 m. The thickness of the zone ranges from 10–15 to 110 m.

Metasomatic rocks demonstrate a clear zoned structure. The following mineralogical zones are distinguished from granite to the following metasomatic deposit.

Zone A. Poorly altered granodiorite. Magmatic paragenesis is the following: Q + $Pl_{25–35}$ + Kfs + Bi + Hbl. Alteration of granodiorite is reflected in the formation of secondary biotite after hornblende and the appearance of small amounts of newly formed muscovite, quartz, chlorite, and epidote. Rocks are characterized by a granitic, porphyric, and medium-granular texture.

Zone B. Strongly altered granodiorite. The main magmatic paragenesis is the same as in Zone A: Q + $Pl_{25–35}$ + Kfs + Bi + Hbl. However, alteration of rocks is much stronger in this zone and results in the appearance of small tables of calcic plagioclase (up to anorthite), abundant muscovite and quartz, epidote, chlorite, and sulfides, mainly pyrite. Tourmaline and andradite–grossular garnet occur in some areas of granodiorite. A primary granite subhedral texture remains in the rocks. The thickness of strongly altered granodiorite zone is *n* m.

Zone C. "Dark-gray" fine-granular metasomatites are represented by massive dark-gray rocks with widely abundant crystals of pink garnet. The rock paragenesis includes Q + Ms + Gr + Kfs + Bt + $Pl_{90–95}$. This rock type is peculiar in the significant content of newly formed plagioclase with the composition close to anorthite. Metasomatites contain small portions of tourmaline, pyrite, pyrrhotite, magnetite, ilmenite, sphalerite, and galena. The zone of metasomatites has a thickness from *n*0 cm to 10 m surrounding the tubular metasomatic deposit at the contact with granite.

Zone D. Ore-bearing "light-gray" metasomatites of the main part of the metasomatic deposit are represented by fine-granular light-gray rocks with small individual pinkish-brown garnet aggregates. Sometimes garnet is accompanied by aggregates of zinc spinel (gahnite). The rock paragenesis is Q + Ms + Gr + Kfs + Bt. Anorthite is absent in these rocks; only small portions of biotite are registered. Small individual aggregates of dark-brown tourmaline are always observed in metasomatites in variable amounts.

The modal composition of samples from all mineralogical zones calculated using the MC software is given in Table 1. This program, description of the algorithm, and examples of calculations, the results of which are given in Table 1, are placed in open access in the information server of the Far East Geological Institute, Far East Branch, Russian Academy of Sciences, http://fegi.ru/institute/innov/461-2013-03-11-03-22-32. Table 1 demonstrates gradual increase of

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Table 1. Modal composition of granodiorites and metasomatites from the Berezitovoe deposit (wt %)

Sample	Zone	Minerals												Σ	Res
		Qtz	Kfs	Plag	Wm	Gr	Bi	Rut	Ep	Apat	Mgt	Ilm	Gbs		
1-B	A	19	7	49.9	1.7	–	10.6	0.2	9.6	0.5	1.3	–	–	99.8	0.00
5	B	25.4	9.5	42.9	10.6	–	8	0.1	1.3	0.3	1.8	0	–	99.9	0.00
8-1	C	40.3	6.0	12.9	26.6	4.5	8.6	–	–	0.3	0.4	0.2	–	99.8	0.03
8-2	D	47.5	–	1.2	49.7	0.4	–	0.1	–	0.0	0.03	–	1	99.9	0.03

Note: Symbols of minerals: Qtz, quartz; Kfs, potassium feldspar; Plag, plagioclase; Wm, muscovite; Gr, garnet; Bi, biotite; Rut, rutile; Ep, epidote; Apat, apatite; Mgt, magnetite; Ilm, ilmenite; Gbs, gibbsite. Res is the residue of the chemical composition of rock not accounted for in the calculated modal composition. The calculation was performed using the MC software (http://fegi.ru/institute/innov/461-2013-03-11-03-22-32).

the quartz and muscovite portions from Zone A to Zone D, which reflects the increase in the intensity of metasomatic process. Peculiarities of the geological structure of the deposit are described in detail in [1].

Analyses of the Pb isotope composition and U–Pb ratios in galena were performed at the Center for Isotope Investigations, Russian Geological Research Institute, using the DUV-193 ablation system, ArF laser COMPex-102 (wavelength 193 nm), and multicollector mass spectrometer with ionization in inductively coupled plasma (ICP-MS) Neptune. The possibility of high-precision analysis of the lead isotope composition using this method was demonstrated in [2] with detailed description of the applied methodology.

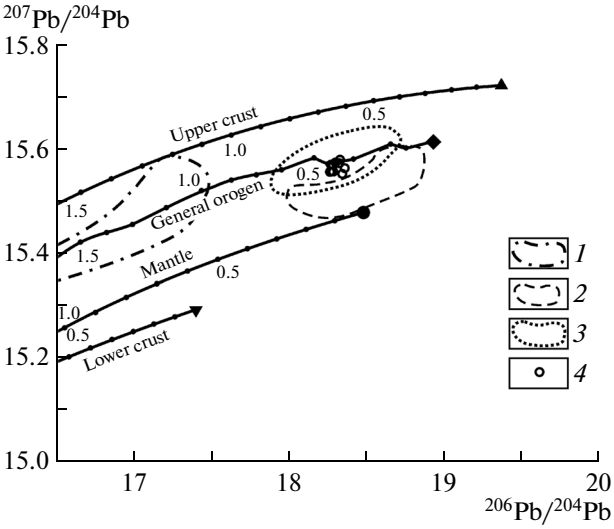

Fig. 1. The diagram of $^{206}Pb/^{204}Pb$–$^{207}Pb/^{204}Pb$ for galena from the Berezitovoe deposit. (*1–3*) Fields of the compositions of lead in galena from the Omolon (*1*), Alazei–Oloi (*2*), and Yano–Kolyma (*3*) provinces of Northeast Russia [4]; (*4*) points of the compositions of galena from the Berezitovoe deposit. Solid lines are the curves of the evolution of lead composition for the upper and lower crust, mantle, and general orogen, according to the model of "Plumbotectonics", ver. IV [5]. Isotope ratios (Ga) are given.

The configuration of collectors for Pb–Pb analyses provided synchronous registration of the isotopes ^{202}Hg–^{203}Tl–$^{204}(Hg + Pb)$–^{205}Tl–^{206}Pb–^{207}Pb–^{208}Pb. Normalization of the measured ratios by the known $^{203}Tl/^{205}Tl$ ratio obtained by measurement of the standard (international standard glass NIST-611) in each individual analytical session was applied for correction of mass discrimination. The absolute values of standard analytical error were 0.02 ($^{206}Pb/^{204}Pb$), 0.016 ($^{207}Pb/^{204}Pb$), and 0.04 ($^{208}Pb/^{204}Pb$).

The isotope analysis of oxygen in silicates and sulfur in sulfides was performed in the Analytical Center, Far East Geological Institute, Far East Branch, Russian Academy of Sciences, in the Laboratory of Stable Isotopes.

$^{18}O/^{16}O$ isotope ratios were measured on a Finnigan MAT 253 isotope mass spectrometer using the laboratory standard calibrated by the international standards NBS-28 and NBS-30. Reproducibility of $\delta^{18}O$ values (1σ) was ±0.2‰, $n = 10$. The weight of analyzed samples was 1–2 mg. The results of $\delta^{18}O$ measurements are given in relation to the international standard VSMOW.

Sample preparation for the mass spectrometric sulfur isotope analysis was performed by the methodology of V.A. Grinenko [3]. The sulfur isotope ratios were measured on a Finnigan MAT 253 isotope mass spectrometer using the dual inlet system and the laboratory standard calibrated against the international standards NBS123, IAEA-S-1, IAEA-S-2, and IAEA-S-3. Reproducibility of $\delta^{34}S$ values (1σ) for international values was ±0.1‰, $n = 10$. The results of $\delta^{34}S$ measurements are given in relation to the international standard VCDT.

The lead isotope composition of galena from different ore types of the Berezitovoe deposit is characterized by close values of the isotope ratios. On the diagram of the lead composition (Fig. 1), they plot in the field of galena from ore formations of the Yano–Kolyma isotope geochemical province, which was distinguished for Northeast Russia together with the

Omolon and Alazei–Oloi provinces on the basis of study of the ore lead isotope composition [4]. According to these data, the substrate of the Yano–Kolyma province includes the Upper Proterozoic and Paleozoic–Mesozoic complexes of the passive continental margin, whereas the Omolon province is represented by the Early Precambrian cratonic block, and the Alazei–Oloi province is represented by the Phanerozoic sedimentary–volcanogenic formations of primitive island arcs and marginal seas.

The model age of lead abruption for the Berezitovoe deposit is expressed by the range of ~330–400 Ma (Fig. 1). According to the previously obtained local U–Pb datings (SHRIMP-II), the age of zircons from metasomatites is 335 ± 4.8 Ma, whereas the age of zircons from ore-hosting porphyric granodiorite is 344 ± 3.3 Ma [6]. The similarity of model ages of galena and zircons, as well as the closeness of the isotope characteristics of ore lead of the Berezitovoe deposit with those of the Yano–Kolyma province, allows us to suggest Paleozoic granite as a source of ore material for polymetallic ores. The origin of this granite resulted from transformation of Proterozoic metamorphic rocks of the basement during the Paleozoic tectonomagmatic cycle.

Stable oxygen isotopes were studied in metasomatic rocks and granites from the deposit (a total of 10 samples). Samples of granites were collected at distances of 10, 5, and 1 m from contact with metasomatites and directly at the contact with the metasomatic zone. Samples of metasomatic rocks were represented by "dark" and "white" metasomatites of the tourmaline–garnet–muscovite–biotite–orthoclase–anorthite–quartz and tourmaline–garnet–muscovite–quartz compositions, respectively.

As is evident from Table 2, the $\delta^{18}O_{SMOW}$ values gradually increase from poorly altered granodiorite towards the center of the metasomatic body. According to the modal composition of rocks (Table 1), the content of quartz in relation to plagioclase, potassium feldspar, biotite, and muscovite increases in the same direction. It is well-known that the sequence of minerals with increasing $\delta^{18}O_{SMOW}$ is the following: biotite–muscovite–calcic plagioclase–sodic plagioclase–potassium feldspar–quartz [7]. Because of this, the increase in the $\delta^{18}O_{SMOW}$ value may easily be explained by the increase in the modal quartz content. The fact of slight and gradual increase of the $\delta^{18}O_{SMOW}$ value from granodiorite to the center of the metasomatic zone provides evidence for the formation of metasomatic rocks directly after host granitoids. However, according to the oxygen isotope composition, the least altered granodiorite (Sample 1-B, Table 1) corresponds to the group of "normal" granitoids [8].

$\delta^{34}S$ in the studied samples of pyrite, sphalerite, and galena mostly collected from polymetallic ores of the Berezitovoe deposit varies within very narrow limits: from +1.2 to –2.1 at an average value of –0.18‰ (Table 3). The narrow range of $\delta^{34}S$ values in sulfides and their closeness to zero provide evidence for the magmatic origin of sulfur [9]. $\delta^{34}S$ values from –4 to +4‰ [10] or from –3 to +3‰ [11] were reported for ore objects related to granitoid magma. The isotope data obtained in this study provide unambiguous evidence for the magmatic origin of sulfur in sulfides.

Table 2. Oxygen isotope composition ($\delta^{18}O_{SMOW}$) in granodiorites and metasomatic rocks of the Berezitovoe deposit

Sample	Rock characteristics	$\delta^{18}O_{SMOW}$
	Zone A	
1-B	Poorly altered granodiorite (10 m from the contact with metasomatites)	8.9
2-B	Poorly altered granodiorite (5 m from the contact with metasomatites)	10.1
3-B	Poorly altered granodiorite (1 m from the contact with metasomatites)	9.7
	Average by the zone	9.6
	Zone B	
5	Granodiorite at the contact with metasomatites	10.0
5-C	Granodiorite at the contact with metasomatites	9.8
	Average by the zone	9.9
	Zone C	
4-A	Dark metasomatite	10.5
4-C	Dark metasomatite	10.4
8-1	Dark metasomatite	10.0
	Average by the zone	10.3
	Zone D	
6	White metasomatite	10.8
8-2	White metasomatite	10.6
	Average by the zone	10.7

Note: Analyses were performed in the Analytical Center, Far East Geological Institute, Far East Branch, Russian Academy of Sciences, on a Finnigan MAT 253 isotope mass spectrometer; analysts E.S. Ermolenko and T.A. Velivetskaya.

The temperatures of sulfide equilibria by the sphalerite–galena (T_1, °C) [12], pyrite–sphalerite (T_2, °C), and pyrite–galena (T_3, °C) thermometers [10] were calculated for five samples. These temperatures range from 294 to 547°C, and two sulfide pairs in Samples 57 and 1514 are characterized by violated isotope equilibrium (Table 3). However, five of nine temperature estimations provide a relatively narrow temperature range from 450 to 550°C that are close to the estimations of P–T conditions of the formation of garnet–muscovite and garnet–biotite mineral equilibria for metaporphyrite dykes and ore-bearing metasomatites (~520°C and 3.5 kbar). The results obtained provide a significant argument in favor of the previously suggested concept on superposed local high-tempera-

Table 3. Isotope composition of pyrite, sphalerite, and galena from ores of the Berezitovoe deposit

Sample	Mineral	$\delta^{34}S_{CDT}$	T_1, °C	T_2, °C	T_3, °C
57	Pyrite	0.2		***	
	Sphalerite	0.9	294	***	
	Galena	−1.4			525
1288	Galena	−1.6			
	Sphalerite	0.2	368		
1294	Pyrite	0.4			
1390	Galena	−1.3			
1503	Galena	−2.1			
1514	Galena	0.0	***		
	Sphalerite	−0.1	***		
ZG-1109	Pyrite	1.2		384	
	Sphalerite	0.5	547		
	Galena	−0.6			480
ZG-1111	Pyrite	1.1		384	
	Sphalerite	0.4	547		
	Galena	−0.7			480

Note: T_1, T_2, and T_3 are the sphalerite–galena [12], pyrite–sphalerite, and pyrite–galena [13] thermometers. *** Violated isotope equilibrium. Analyses were performed in the Analytical Center, Far East Geological Institute, Far East Branch, Russian Academy of Sciences, on a Finnigan MAT 253 isotope mass spectrometer; analysts V.M. Avchenko, N.P. Konovalova, and T.A. Velivetskaya.

ture metamorphism of ore-bearing garnet-rich rocks in the tubular ore body of the Berezitovoe deposit.

As a whole, the reported data on the composition of lead, oxygen, and sulfur isotopes in rocks and ores of the Berezitovoe deposit, as well as the previously obtained data on the U–Pb age of zircons from granodiorites and metasomatites, allow us to consider that metasomatic rocks of the deposit composing the fluid–explosive structure were formed directly after host Paleozoic granitoids. The high estimated temperatures of sulfide equilibria calculated by sulfur isotope ratios in mineral pairs of galena–sphalerite, pyrite–sphalerite, and pyrite–galena support the previously suggested idea on superposed local metamorphism of metasomatites and ores within the tubular structure. The lead isotope composition in polymetallic ores of the deposit may provide a basis for the conclusion on the Middle Paleozoic age of their source.

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