Crustal Source of Pb and S at the Yubileynoe Porphyry Gold Deposit (Southern Urals, Kazakhstan): High Precision Pb–Pb and $\delta^{34}\text{S}$ Data

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Abstract—The Yubileynoe large gold deposit, located at the southern end of the Magnitogorsk megazone, is the only known representative of the Au–porphyry systems in the Southern Urals. It is genetically related to granitoids formed in a suprasubduction setting under mature oceanic island arc environment/setting. The obtained isotope (Pb–Pb and $\delta^{34}\text{S}$) data indicate the input of mineral-forming components into the Au–porphyry system of the deposit, mainly from granitoid melts, confirming a common source of ore material and ore-bearing granitoids. The geochemical and isotopic characteristics of granitoids indicate the leading role in their genesis of the crustal source, which is considered Late Precambrian continental crust.

Keywords: Au–porphyry systems of the Urals, Yubileynoe deposit, sources of material, Pb and S isotope data

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INTRODUCTION

Deposits of the porphyry family, which play a leading role in the global production of Cu, Mo, Au, Ag, and Re, are formed in various geodynamic settings: suprasubduction, collisional, and postcollisional (Richards, 2009; Sillitoe, 2010; etc.). The diversity of geodynamic settings presupposes the involvement in ore-forming processes of sources of material differing in geochemical nature. Their identification and assessment of their role in the genesis of specific porphyry-type deposits is one of the most pressing issues in the developed genetic models (Sillitoe and Hart, 1984; Bouse et al. 1999; Shafiei, 2010; Plotinskaya et al., 2017a; Shen et al., 2018; etc.).

In existing genetic models describing the formation of porphyry deposits, various sources of metals and volatile components are considered: rocks of subducted oceanic crust, oceanic sediments, metasomatized mantle from the mantle wedge, as well as the asthenospheric and metasomatized subcrustal lithospheric mantle (Sillitoe and Hart, 1984; Bouse et al. 1999; Shafiei, 2010; Richards, 2011; etc.). It is believed that metasomatized mantle of the mantle wedge plays a leading role in the input of metals and volatile components into Cu–porphyry systems associated with a suprasubduction setting (Richards, 2011 and references therein). Conversely, in collisional settings in

which Cu–Mo, Mo, and Au porphyry deposits are formed, continental crust makes a significant contribution, but the participation of a mantle source is not excluded.

Several dozens porphyry-type deposits and ore occurrences are known in the Urals (Grabazhev and Belgorodsky, 1992; Seravkin et al., 2011; Seravkin and Kosarev, 2019; Andreev et al., 2018; Minina and Migachev, 2018; Plotinskaya et al., 2017b). Mainly, these are Cu-, Mo- or Au–porphyry and Cu–skarn–porphyry objects. Their formation took place over a long time period (from the Silurian to Late Carboniferous) (Grabazhev et al., 2017; Tessalina and Plotinskaya, 2017) in oceanic island arcs and active continental margin settings, as well as in collision processes (Plotinskaya et al., 2017b). Despite the extensive geological, geochemical, and isotopic dataset on ore mineralization and ore-forming rocks, the question of the source/sources of material in the porphyry systems of the Urals remains controversial (Grabazhev, 2009; Plotinskaya et al., 2017a; etc.).

One of the largest Au–porphyry deposits in the Urals is the Yubileynoe (formerly known as Shekarabulak-II), located in western Kazakhstan and discovered in 1961 (Bespaev et al., 1997). According to the 2015 data from the mining company AO AltynEx for, the balance category $C_1 + C_2$ reserves of the deposit

amounted to 41 109.5 thousand tons with an average content of 2.07 ppm Au, 2.15 ppm Ag, and 0.156% Cu, i.e., about 85 t Au (AO AltynEx Company, 2015).

To date, the geological structure of the deposit and the mineral and chemical composition of metasomites and ores have been characterized (Narwaith et al., 1974; Abdulin et al., 1976; Shatov et al., 2014; Plotinskaya et al., 2018; Plotinskaya, 2020; etc.), the geochemical features of ore-bearing granitoids have been studied (Grabezhev and Belgorodsky, 1992), and isotope studies (Nd, Sr, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and $\delta^{34}\text{S}$) of ore and gangue minerals, as well as ore-bearing granitoids, have been carried out (Grabezhev et al., 1989; Grabezhev, 2009; Shen et al., 2018).

Based on the results of these studies, it was suggested that the formation of ore-bearing melts occurred at the upper mantle–continental crust boundary (less than 40 km) and is associated with the initial melting of juvenile mantle material, which was accompanied by processes of fractional crystallization and contamination of melts with ancient crustal material (Grabezhev, 2009; Shen et al., 2018). At the same time, researchers have not considered the role of mantle and crustal sources of material that directly took part in ore-forming processes.

In modern studies of porphyry-type deposits, a wide range of isotope geochemistry methods are used to identify sources of ore components, including the Pb–Pb method. Studying the Pb–Pb isotopic characteristics of porphyry mineralization is one of the most effective approaches to reliably identify genetic relationships between igneous rocks and ores and determine the role of mantle and crustal sources in their genesis (Bouse et al. 1999; Kouzmanov et al., 2009; Shafiei, 2010; Borba et al., 2016; Huston et al., 2016; Plotinskaya et al., 2017a; etc.).

In this article, in order to identify the source(s) of lead and sulfur and assess their role in the formation of the Yubileinoe Au–porphyry deposit, we conducted a comprehensive study of the Pb and S isotopic composition in pyrite of the ore mineralization, as well as the Pb–Pb isotopic characteristics of ore-bearing granitoids. Lead isotopic analysis was performed using multiple-collector mass spectrometry with inductively coupled plasma in its high-precision option (MC-ICP-MS). This makes it possible to record small (0.05–0.1%) variations in Pb isotopic ratios in geological objects, reveal correlations against their background, and reliably compare the Pb–Pb isotopic characteristics of ores and igneous rocks.

BRIEF GEOLOGICAL DESCRIPTION OF THE DEPOSIT

The Yubileinoe deposit is located in the south of the Magnitogorsk volcanic megazone in the Urals in the West Mugodzharsk zone (Fig. 1a). Among the country rocks, the most widespread are Early–Middle

Devonian volcanic rocks of the tholeiitic series (Mugodzharsk Formation), overlain by Middle Devonian volcanosedimentary rocks of the island arc series (Fig. 1b). The volcanic sequences are crosscut by Late Devonian–Early Carboniferous intrusions of mafic, intermediate, and felsic compositions, attributed to the Ayryuk Complex (Narwaith et al., 1974; Abdulin et al., 1976; Grabezhev, 2009; Shatov et al., 2014). The porphyry mineralization is associated with a small (about 400 m in diameter) stock of plagiogranite porphyry with an age of 374 ± 3 Ma (Grabezhev, 2014). In their geochemical characteristics (average contents of $\text{Rb} = 46 \pm 22$, $\text{Nb} = 5.6 \pm 1.5$, $\text{Y} = 9.6 \pm 2.2$, and $\text{Ta} = 1.1 \pm 0.6 \mu\text{g/g}$), the rocks are close to granitoids formed both in collisional and volcanic island arc settings (Plotinskaya et al., 2017b; Shen et al., 2018; our unpublished data).

According to the available geotectonic reconstructions for the South Urals, the formation of the Yubileinoe field could have occurred in the setting of a mature oceanic island arc or in the conditions of an early stage of its collision with the East European continent (Puchkov, 2010; Samygin and Burtman, 2009; etc.).

The ore mineralization is represented by quartz–sulfide and sulfide veinlets 0.5–1 cm thick, which form stockwork zones confined mainly to exo- and endomorphic intrusion contacts. Among the ore minerals, pyrite, chalcopyrite, and magnetite predominate. Bornite, molybdenite, arsenopyrite, sphalerite, galena, and native gold are present in subordinate quantities. Rare minerals include scheelite, sulfosalts, and Bi and Pb sulfotellurides. The ore mineralization formed in two stages: early quartz–magnetite–hematite and late chalcopyrite–pyrite (Abdulin et al., 1976; Plotinskaya et al., 2018; Plotinskaya, 2020).

MATERIALS AND METHODS

Sampling

The isotopic composition of lead and sulfur was studied in pyrite from late chalcopyrite–pyrite mineralization with native gold. The pyrite was separated from thin (0.5–1 cm) quartz and quartz–carbonate veinlets localized both in ore-bearing granitoids and in basalts (Figs. 2a, 2d).

The pyrite hosts numerous microinclusions of magnetite, chalcopyrite, and galena (Fig. 2e), as well as Bi and Pb sulfosalts (Plotinskaya, 2020). The analyzed feldspar fractions were represented by plagioclase from plagiogranite–porphyry, which makes up the bulk of the massif, as well as potassium feldspar from late granite micropegmatite veins (Figs. 2b, 2c). The studied plagiogranite–porphyries show signs of metasomatic alteration, which are primarily expressed as sericitization and albitization of plagioclase phenocrysts (Fig. 2f). These processes are manifested most intensely in sample Yub-1105/452.

Fig. 1. (a) Position of the Yubileinoe porphyry gold deposit (Kazakhstan) on tectonic sketch map of Southern Urals; (b) geological sketch map of the Yubileinoe deposit after (Narwaith et al., 1974). (1) Meso–Cenozoic cover; (2) Pre-Ural foredeep; (3) sialic (a) and volcanic (b) megazones of Southern Urals (WU, Western Ural; M, Magnitogorsk; EU, East Ural volcanic; TU, Trans-Ural); (4) boundaries of Southern Ural megazones; (5) tholeiitic basalts (D_{1-2}); volcano-sedimentary rocks (D_{2-3}) of island arc origin; (6) granitoids ((a) biotite–plagiogranite–porphyry, (b) biotite–amphibole plagiogranite–porphyry) of Ayryuk intrusive complex (D_3-C_1); (7) ore stockwork.

Fig. 2. Macro- (a–c) and microphotographs (d–f) of ore and rock samples of Yubileinoe porphyry gold deposit (Kazakhstan); (a) quartz veinlets with sulfide mineralization in basalts (sample Yub-1121/300); (b) plagiogranite–porphyry (sample Yub-1105/452); (c) granite micropegmatite in plagiogranite–porphyry (sample Yub-1121/337); (d) pyrite disseminations in vein quartz, reflected light (sample Yub-1121/374); (e) microinclusions of galena and sphalerite in pyrite, BSE image (sample Yub-1121/351); (f) plagioclase phenocrysts among quartz–feldspar groundmass of plagiogranite–porphyry (transmitted light, crossed nicols) (sample Yub-1105/628). Py, pyrite; Gn, galena; Sp, sphalerite; Pl, plagioclase; Mu, muscovite.

Analytical Methods

The isotopic composition of Pb and S was studied at the laboratory of isotope geochemistry and geochronology of IGEM RAS.

Pb isotope analysis was performed for monomineralic fractions of pyrite and feldspars of ore-bearing granitoids. The sample weights were 0.02–0.03 g for pyrite and 0.05–0.07 g for feldspar. Before chemical decomposition, pyrite and feldspar were treated with a weak solution of nitric acid (3 and 10%, respectively) to remove lead contamination from the surface of the grain. Chemical preparation of samples, as well as chromatographic separation of Pb, were carried out according to the method described in (Chugaev et al., 2013). The lead fractions obtained after ion exchange chromatography were dissolved in 3% HNO₃. The total blank for the chemical procedure did not exceed 0.1 ng Pb. Mass spectrometry measurements were performed on a NEPTUNE multicollector mass spectrometer in the wet plasma mode after (Chernyshev et al., 2007). Solutions with a Pb concentration of 100–400 ng/g were analyzed. Immediately before measurement, the solutions were traced with thallium. Mass-bias correction for the measured Pb isotope ratios was performed using the reference ratio $^{205}\text{Tl}/^{203}\text{Tl} = 2.3889 \pm 1$ employing an exponential law. The accuracy of the obtained Pb–Pb data was controlled by the results of parallel analyzes of the Pb isotopic composition standard SRM-981 and the AGV-2 and BCR-1 standard rock samples of the USGS. Total analytical error for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios did not exceed $\pm 0.02\%$.

Sulfur isotope analysis was carried out in pyrite samples with a weight of ~0.14 mg. Sulfur was converted to gaseous SO₂ using an FlashHT 1112 elemental analyzer at 1020°C in a reactor filled with Cu⁰ and WO₃. Samples and standards in tin capsules were sequentially introduced into the reactor using an autosampler. The sulfur isotopic composition in SO₂ gas was measured by CF-IRMS on a DELTAV + mass spectrometer (Finnigan). $\delta^{34}\text{S}$ was calibrated against three international standards, IAEA-S-1 (–0.3), IAEA-S-3 (–32.55‰) and NBS-127 (+21.1 ‰), which were analyzed simultaneously with the samples. The results obtained are expressed in the international scale V-CDT (Vienna Canyon Diablo Troilite):

$$\delta^{34}\text{S}_{\text{sample}} = \left[\left(\frac{^{34}\text{S}}{^{32}\text{S}} \right)_{\text{sample}} / \left(\frac{^{34}\text{S}}{^{32}\text{S}} \right)_{\text{VCDT}} - 1 \right] \times 1000.$$

The reproducibility of the results in a series of parallel measurements of standard samples was ± 0.25 ‰ ($\pm 1\sigma$).

In order to calculate the initial Pb isotopic ratios in the same weighed portions of monomineralic fractions for which the Pb isotopic composition was measured, data on the concentrations of Pb, Th, and U were

obtained. The concentrations of these elements were measured by ICP-MS from solutions on an iCAP SQ ICP-MS inductively coupled plasma mass spectrometer (Thermo Scientific) at the laboratory of isotopic and elemental analysis of IGINT KFU. The error in determining the Pb, Th, and U contents in the samples, estimated from the results of systematic analyses of standard rock samples BHVO-2 and AGV-2 of the USGS, did not exceed $\pm 3\%$ ($\pm 2\text{SD}$).

RESULTS

Table 1 lists the measured Pb isotopic ratios, $\delta^{34}\text{S}$ values, and data on the Pb, Th, and U contents in pyrite and feldspars.

U–Th–Pb Systematics of Granitoid Pyrite and Feldspars

The Pb isotopic composition, as well as data on the Pb, Th, and U concentrations, were obtained for six pyrite samples from the ore stockwork and four samples of feldspars of ore-bearing granitoids from the Yubileinoe deposit. Pyrites from sulfide veinlets are generally characterized by high Pb contents, which vary in a wide range from 9.8 to 1840 ppm. Such a significant heterogeneity of the studied pyrite samples in Pb content is due to the uneven presence of lead and bismuth sulfotellurides microinclusions in the mineral (Plotinskaya, 2020), as well as galena (Fig. 2e). Conversely, the Th and U concentrations in pyrite turned out to be low. For most of the samples, the Th content is below the detection limit, while the maximum value was 0.03 ppm. The U content is slightly higher than the detection limit and lies in the range of values from 0.01 to 0.07. Varying high Pb concentrations at low and sufficiently sustained Th and U contents determine low values of the ratios $^{232}\text{Th}/^{204}\text{Pb}$ and $^{238}\text{U}/^{204}\text{Pb}$, which do not exceed 0.007 and 0.052, respectively. Taking into account these data, the correction of the measured values of isotope ratios $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ for an age of 374 Ma does not exceed 0.02%, i.e., within the analytical error of measuring these ratios.

Feldspars of ore-bearing granitoids have Pb contents typical of these minerals varying from 9.1 to 53 µg/g. The highest value was obtained for the fraction of potassium feldspar sampled from late granite micropegmatite. The measured Th and U concentrations vary from 0.3 to 2.5 and from 0.6 to 2.1 ppm, respectively. The elevated Th and U contents, in turn, determine the high $^{232}\text{Th}/^{204}\text{Pb}$ and $^{238}\text{U}/^{204}\text{Pb}$ ratios in feldspars. In this case, the $^{232}\text{Th}/^{204}\text{Pb}$ values vary within narrow limits (2.1–3.1), while for $^{238}\text{U}/^{204}\text{Pb}$, the range of Pb ratios is several times wider, from 1.3 to 15. As a consequence, the correction of the $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios for an age of 374 Ma for all feldspar samples significantly exceeds the analytical error, 0.15 and 5%, respectively. After correction, the isoto-

Table 1. Pb and S isotopic composition data in sulfides from gold–porphyry mineralization of Yubileinoe deposit and in feldspars of ore-bearing granitoids

Sample no.	Characteristics:	Pb, ppm	Th, ppm	U, ppm	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$\delta^{34}\text{S}$
<i>gold–porphyry mineralization</i>								
Yu-1105/430	Pyrite, pyrite-chalcopryrite vein in plagiogranodiorites	275	<DL	0.010	18.4207	15.6562	38.3583	8.4
Yu-1105/470	Same	54	<DL	0.015	18.4344	15.6554	38.3493	9.2
Yu-1121/300	Pyrite, quartz vein with pyrite, chalcopryrite, chlorite and epidote in basalts	9.8	<DL	0.008	18.4221	15.6547	38.3469	9.7
Yub-1121/351	Same	278	0.03	0.034	18.4161	15.6578	38.3586	7.6
Yub-1121/365	Pyrite, carbonate–pyrite vein in plagiogranodiorites	755	0.012	0.069	18.4126	15.6587	38.3612	8.7
Yub-1121/374	Pyrite, quartz–pyrite veins in dolerites	1840	<DL	0.037	18.4102	15 to 6564	38.3520	8.8
<i>Ore-bearing granitoids</i>								
Yub-1105/452	Plagioclase, plagiogranite–porphyry	9.1	0.29	2.1	19.3179	15.7007	38.3946	
Yub-1105/628	Same	36	1.4	0.74	18.5218	15.6624	38.4052	
Yub-1121/336	Same	16.6	0.55	0.64	18.5774	15.6614	38.3915	
Yub-1121/337	K-feldspar, granite micropegmatites	53	2.5	1.2	18.5802	15.6639	38.4136	

The table lists the measured Pb isotopic ratios. <DL, below detection limit.

pic composition of Pb in feldspars turned out to be more homogeneous, and the values of isotopic ratios change in the following ranges: for $^{206}\text{Pb}/^{204}\text{Pb}$ —18.43–18.49, $^{207}\text{Pb}/^{204}\text{Pb}$ —15.652–15.659, $^{208}\text{Pb}/^{204}\text{Pb}$ —38.351–38.357. In this case, geochemically significant variations (i.e., exceeding the analytical error) are only variations in the ratio $^{206}\text{Pb}/^{204}\text{Pb}$. In the case of a the $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios, the scatter of values, estimated from the value of the variation coefficient, is equal to or less than the analytical error. Despite such a small scale of variations, it can be seen from the obtained Pb–Pb data that the most radiogenic initial isotopic composition of lead in terms of isotope content ^{206}Pb is found in late pegmatoid veins, while in ore-bearing plagiogranite–porphyry, the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio is systematically lower and lies in a narrow range from 18.425 to 18.443, for which the difference in extreme values is only 0.05%.

$\delta^{34}\text{S}$ Values in Pyrite

The sulfur isotopic composition in the studied pyrite samples is relatively uniform. High positive $\delta^{34}\text{S}$ values were obtained for this mineral, varying from +7.6 to +9.7‰. In this case, no correlation was found between the $\delta^{34}\text{S}$ value in pyrite and geological and/or mineralogical characteristics of the sample. The data

presented in this work are consistent with previously published results of similar studies (Grabezhev et al., 1989), who reported that $\delta^{34}\text{S}$ values for pyrite from the ore stockwork of the Yubileinoe deposit vary from +8.5 to +9.0‰ (three samples).

DISCUSSION

Sources of Pb in Ores and Rocks

Spatial association of ore and granitoids at the Yubileinoe deposit suggests their genetic relationship and a single source of material (Grabezhev, 2009; Shatov et al., 2014; etc.). Therefore, it is of interest to compare the isotopic composition of Pb ores with that in granitoids and to assess the role of felsic magmatic melts in Pb input to the mineral-forming system of the deposit. Figure 3 shows that pyrite from the ore stockwork and plagioclase of plagiogranite–porphyry are very similar in Pb isotopic composition. Some of the points of pyrite fall in the field of ore-bearing granitoids. However, despite the similarity of the Pb isotopic ratios of ores and igneous rocks and the small scale of variations, there are distinct differences: the points of ore lead are systematically shifted to the left of the of isotopic composition field of Pb granitoids and form short trends in both diagrams, which, based on their position, can be interpreted as mixing trends. The

Fig. 3. Pb–Pb diagrams for Pb isotopic composition of pyrite and feldspars of granitoids from Yubileinoe gold–porphyry deposit (Kazakhstan). Diagrams show Pb isotopic ratios corrected for 374 Ma. Gray line shows trend of isotopic composition of ore Pb; dashed line shows isotopic composition field of Pb plagioclases of plagiogranite–porphyry ore-bearing stock. Analytical errors: for pyrite, $\pm 0.01\%$ (SD); for feldspars, $\pm 0.015\%$ (SD).

relationship between the trends and isotopic composition fields of Pb granitoids indicates that felsic magmatic melts were one of the sources of lead in ores and their contribution was decisive. At the same time, Pb input from another source has also been established. Its contribution was insignificant, and the lead in it had a reduced ^{206}Pb content and, conversely, elevated concentrations of ^{207}Pb and ^{208}Pb .

According to the Stacy–Kramers model (Stacey and Kramers, 1975), the source of material of ores and magmatic melts at the Yubileinoe deposit was characterized by elevated values of with respect to the mean crustal values μ_2 ($^{238}\text{U}/^{204}\text{Pb}$) = 9.92 ± 0.01 and ω_2 ($^{232}\text{Th}/^{204}\text{Pb}$) = 38.03 ± 0.10 . The values of the Pb–Pb model age (T_m = 260–280 Ma) reflecting the esti-

mated time of Pb separation from the U–Th–Pb isotope system of the source proved, on average, 100 Ma younger than the geological age of the deposit. This discrepancy indicates that shortly before Pb separation from the U–Th–Pb system as a result of magmatic and ore-forming processes, there was a change (increase) in the U/Pb ratio in the source, e.g., due to metasomatic or metamorphic alteration of crustal rocks.

On the plots, point corresponding to K-feldspar of late pegmatoid veins is to the right of the field of ore-bearing plagiogranite–porphyry. The observed ratio of the Pb isotopic composition of rocks allows us to conclude that the studied granitoids had a common source of magmatic melts in their U–Th–Pb characteristics. In this case, the shift with respect to $^{206}\text{Pb}/^{204}\text{Pb}$ in granite micropegmatites is explained by accumulation of ^{206}Pb in the source during the time that separates the formation of the plagiogranite–porphyry stock and intersecting granite micropegmatite veins. Based on this assumption, it is possible to estimate the duration of the evolution of the Pb isotopic composition in the source, taking for μ_2 a value of 9.92 and Δ ($^{206}\text{Pb}/^{204}\text{Pb}$) = 0.061. From the calculations, it follows that the formation of late granite micropegmatite veins was separated from plagiogranite–porphyry by no more than 40 Ma.

Figure 4 shows the average crustal growth curve according to the Stacy–Kramers model and the curves of evolution of the isotopic composition of Pb in various crustal reservoirs of the Earth according to the Zartman–Doe model (Zartman and Doe, 1981). For comparison, the isotopic composition fields of Pb ore of the Silurian epithermal and porphyry deposits of the East Ural volcanic megazone and Early Devonian Cu–porphyry deposits of the Magnitogorsk megazone are also plotted (Plotinskaya et al., 2017a; Chugaev et al., 2019). Their formation is associated with oceanic island arcs of different ages. Additionally, Pb–Pb data are given for suprasubduction Late Paleozoic (D_3 – C_1) granitoids of the Chelyabinsk pluton (East Ural megazone) (Plotinskaya et al., 2017a) and the Mindyak gold deposit (Magnitogorsk megazone), close to them in age, localized among rocks of a black shale formation (Chugaev and Znamensky, 2018). The latter show the Pb–Pb isotopic characteristics of the regional crustal reservoir for the Southern Urals in the Late Devonian–Early Carboniferous, to which the Yubileinoe deposit is similar in age.

On both graphs, the points of the isotopic composition of Pb ores and granitoids of the Yubileinoe deposit form compact fields (Figs. 4a, 4b). On the diagram with “uranogenic” Pb isotopes (Fig. 4b), the points are located near the upper crustal evolutionary curve, while in $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{208}\text{Pb}/^{204}\text{Pb}$ coordinates (Fig. 4a), they lie above the average crustal growth curve and crustal reservoir curves (upper crust and orogen). The points corresponding to the Yubileinoe deposit are located outside the fields of the Pb isotopic

Fig. 4. Pb–Pb diagrams for porphyry and epithermal deposits and rocks of Southern Urals. Diagrams show Pb isotope ratios corrected for age of deposits. S–K, evolutionary curves according to Stacy–Kramers model (Stacey and Kramers, 1975); solid lines, curves of Pb isotopic composition evolution in crustal geochemical reservoirs of Earth according to Zartman–Doe model (Zartman and Doe, 1981).

composition of Cu–porphyry and epithermal deposits of the East Ural volcanic and Magnitogorsk megazones, for which the participation of a mantle source has been suggested (Grabezhev, 2009; Plotinskaya et al., 2017a). The Yubileinoe deposit also has Pb–Pb isotopic characteristics similar to the suprasubduction granitoids of the Chelyabinsk pluton and gold mineralization of the Mindyak deposit, in which lead had predominantly crustal origin.

These features, as well as the values of the model parameters (μ_2 , ω_2), indicate that the lead of ore and rocks of the Yubileinoe deposit had a crustal source. In turn, the ratio of the Pb isotopic composition fields of the Yubileinoe deposit and porphyry–epithermal deposits of the East Ural and Magnitogorsk megazones indicate the predominant role of crustal lead in the Au–porphyry mineralization. This conclusion agrees with the results of an Sm–Nd study of ore-bearing plagiogranite–porphyry and their chemical characteristics (low Cr (7–12 ppm) and Ni (8–15 ppm) concentrations and low Nb/Ta = 8.1–8.7) (Grabezhev, 2009; Shen et al., 2018). The obtained negative of ϵ_{Nd} (–2.6...–2.9) values and Proterozoic (1.3–1.4 Ga) model (T_{DM2}) Nd ages (Shen et al., 2018) indicate the formation of granitoid melts as a result of melting of Proterozoic crust.

Sources of Sulfur

For the Yubileinoe deposit, a narrow range of variations in $\delta^{34}\text{S}$ (+7.6 to +9.7‰) has been established that is typical of porphyry deposits in various regions of the world, (He et al., 2020; Hutchison et al., 2020). In the Southern Urals, within individual porphyry deposits, variations in $\delta^{34}\text{S}$ also do not exceed 2–3‰; however, these values themselves (–1.5 to +5.7‰) are significantly lower than those obtained for the Yubileinoe deposit (Grabezhev et al., 1989). Thus, the Yubileinoe deposit is characterized not only by homogeneous sulfur isotopic characteristics, determined by its fluid transfer (Dubinina et al., 2010), but also elevated $\delta^{34}\text{S}$ values, which is unusual compared to analogous fields. If fluid transfer of ore components for porphyry-type deposits is not in doubt, then the mechanism leading to deposition of isotope-enriched ^{34}S sulfides requires discussion, since at least two reasons of the appearance of similar sulfur isotopic characteristics are possible. Fundamentally, these reasons differ in the role of host rocks as one of the sources of sulfur in the ore-forming fluid. Isotope-weighted reduced sulfur in the ore-forming system can be either a product of sulfur entrainment from surrounding rocks, or the result of a change in redox conditions in the evolution of the fluid system.

In the first case, with an insignificant role of sulfur redox processes during its extraction and further evolution of the fluid system, it is possible to estimate the approximate amount of sulfur extracted from the sur-

rounding rocks. For $\delta^{34}\text{S}$ of the magmatic source of sulfur close to zero and a $\delta^{34}\text{S}$ value for sulfur of the host Devonian volcano–sedimentary rocks corresponding to the sulfur isotopic composition of Devonian marine sulfate (23‰, (Canfield and Farquhar, 2009)), it is necessary to extract about 40% of sulfur from the surrounding rocks in the fluid in order to yield the observed range of $\delta^{34}\text{S}$ in sulfides of the Yubileinoe deposit.

An alternative variant implies a change in the sulfur oxidation state at different stages in the evolution of the fluid ore-forming system. In the absence of sulfur from surrounding rocks, the possible formation of sulfide minerals with high $\delta^{34}\text{S}$ values will depend on the form of sulfur in the magmatic melt, which is determined primarily by the oxygen fugacity. If $f\text{O}_2$ exceeds the values that determine the sulfide–sulfate barrier (Markl et al., 2010), then oxidized sulfur predominates in the melt. In this case, the separation of the fluid containing SO_2 with a sulfur isotopic composition $\delta^{34}\text{S}(\text{SO}_2)^0$ and its further cooling with an increase in the $\text{H}_2\text{S}/\text{SO}_2$ ratio (Rye, 2005; Richards, 2011) cannot lead to the appearance of $\delta^{34}\text{S}$ sulfide sulfur values exceeding the initial values of $\delta^{34}\text{S}(\text{SO}_2)^0$. Since ^{34}S in the entire temperature range is distributed in favor of oxidized sulfur (Eldridge et al., 2016), sulfides precipitated from such a fluid usually have zero or small negative $\delta^{34}\text{S}$ (Rye, 2005; Richards, 2011; etc.).

However, if $f\text{O}_2$ ensures the presence of sulfur in the melt in the form of an S^{2-} particle, and sulfur leaves the fluid in the form of SO_2 , the situation may be the opposite. At the moment of fluid separation, sulfur fractionation occurs, which is determined by the temperature of the process, as a result of which the $\delta^{34}\text{S}(\text{SO}_2)^0$ values can vary within fairly wide limits. Figure 5 shows the calculation of $\delta^{34}\text{S}(\text{SO}_2)^0$ values depending on the temperature of fluid separation and initial isotopic composition of magmatic sulfur (for the calculation, the initial values were $\delta^{34}\text{S} = 0$, +2, and +4‰). The vertical dotted line limits the range of $\delta^{34}\text{S}$ values observed in sulfides of the Yubileinoe deposit. As follows from the calculation from the thermometric dependences (Eldridge et al., 2016), for zero values of $\delta^{34}\text{S}$ of magmatic sulfur, fluid separation could have occurred in the range 300–370°C. For magmatic sulfur with $\delta^{34}\text{S} = +2$ ‰, the fluid could have separated at 370–480°C, and for $\delta^{34}\text{S} = +4$ ‰, already at 480–670°C. In this model, it is assumed that as the fluid cools, a rapid change in P–T conditions occurs, as a result of which nearly all oxidized sulfur is quantitatively reduced and does not undergo subsequent exchange with other sulfur-containing phases. This mechanism was proposed in a study of sulfur isotopic variations in ore sulfides of the Akchatau deposit (Dubinina et al., 1995). Its realization undoubtedly

Fig. 5. Calculated lines of variation of $\delta^{34}\text{S}(\text{SO}_2)^0$ as function of temperature of separation of magmatic fluid. Numerals on lines are initial $\delta^{34}\text{S}$ values of magmatic sulfur. Dotted line, range of $\delta^{34}\text{S}$ in sulfides of Yubileinoe deposit. Calculation was done according to equations after (Eldridge et al., 2016).

requires fulfillment of a number of conditions, first of all, predominance of S^{2-} .

The low sulfur content in apatite from granites of the Yubileinoe stock and, conversely, high sulfur content in biotite (Grabezhev and Voronina, 2012) suggests that the predominant form of sulfur in the melt was S^{2-} (Tang et al., 2020). In turn, infiltration of the fluid into heated mafic host rocks containing a significant amount of ferrous iron should lead to abiogenic sulfate reduction, i.e., quantitative conversion of all oxidized sulfur contained in the fluid into reduced form (Canfield and Farquhar, 2009). Thus, the above-described mechanism for the occurrence of elevated $\delta^{34}\text{S}$ values in sulfides could have occurred during formation of the Yubileinoe deposit.

It should be noted that we should not exclude a combination of the two above-mentioned mechanisms of the formation of sulfides with high $\delta^{34}\text{S}$ at the deposit. During formation of an ore stockwork in tholeiitic basalts during thermogenic reduction of sulfur, its partial extraction from the host rocks could occur. A similar process usually takes place during thermogenic reduction of seawater sulfate in convective hydrothermal systems (Dubinina et al., 2020).

The participation of material from a nonmagmatic source in ore-forming processes is indicated by the relationship between the $\delta^{34}\text{S}$ values with the $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios (Figs. 6a, 6b). From the direction of the coordinated change in these values, it follows that the isotopic composition of sulfur in this source

Fig. 6. Comparison of $\delta^{34}\text{S}$ values and $^{208}\text{Pb}/^{204}\text{Pb}$ (a) and $^{207}\text{Pb}/^{204}\text{Pb}$ (b) ratios of pyrite from Yubileinoe gold-porphyry deposit (Kazakhstan). Diagrams show Pb isotopic ratios corrected for 374 Ma. Trends of $\delta^{34}\text{S}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios are shown in gray. Analytical uncertainties ($\pm 0.01\%$, SD) are indicated for Pb isotopic ratios. For $\delta^{34}\text{S}$, error is less than size of symbol.

should be characterized by the value $\delta^{34}\text{S} < 7.6\text{‰}$. The position of the Pb–Pb trends on the isotope diagrams (Figs. 4a, 4b) suggests that the additional Pb input came from a source with high values of μ_2 (> 9.94) and ω_2 (> 38.2).

The role of a Crustal Source in the Gold Ore Mineralization

Gold-bearing porphyry mineralization in most deposits is associated with acidic calc-alkaline and subalkaline melts, which formed in collisional or suprasubduction (Andean type) settings as a result of melting of continental crust. Compared to typical suprasubduction Cu-porphyry deposits of oceanic island arcs, the fluid in such porphyry systems is in a more oxidized state, which facilitates Au transport from the source enriched with ore components and its deposition at the mid- and upper levels of the lithosphere (Richards, 2011). In this case, as a result of

interaction of ore-bearing melts and fluids with host rocks, continental material crust is entrained, proved by the results of a lead isotope study of Cu–(Au)–Mo–porphyry deposits in different regions of the world, differing in age and geotectonic formation setting (Kouzmanov et al., 2009; Chugaev et al., 2013; Borba et al., 2016; Zang et al., 2016; etc.). As a rule, continental crust of the tectonic block hosting the deposit is considered the crustal source of lead in such studies. The contribution of material from an enriched mantle source has also been established, although its contribution to the overall lead input balance is of lesser importance. A distinctive feature of the Yubileinoe deposit is the dominant role of a crustal source for ore and magmatic lead. This conclusion, as well as the available geochemical and isotope characteristics of ore-bearing granites, which are close to syncollisional granitoids, suggest that the formation of the Yubileinoe deposit is associated with the onset of collisional processes in the Southern Urals in the Late Devonian.

CONCLUSIONS

Generalization of the available isotope dataset for ores and rocks of the Yubileinoe Au–porphyry deposit, including the present results of, allows us to conclude the following.

(1) The input of Pb to the Au–porphyry system of the Yubileinoe deposit mainly originated from silicic magmas that formed plagiogranite–porphyries. Pb–Pb isotope data directly confirm a common source for ores and ore-bearing granitoids, which agrees with the previously proposed model of genesis of the Yubileinoe deposit (Grabezhev, 2009). As well, the entrainment of lead in ore-forming processes from another source has been established for the first time, which could have been the host rocks. However, the contribution of this source to the overall balance of ore lead was minimal.

(2) The formation of ore-generating granitoid melts occurred due to melting of relatively ancient (Late Precambrian) continental crust, which included metamorphic rocks.

The latter conclusion does not agree with the concept of generation of ore-bearing melts at the upper mantle–continental crust boundary due to melting of the mafic substrate (Grabezhev, 2009; Shen et al., 2018). Our results, conversely, indicate the dominant role of a crustal source in the genesis of Au–porphyry mineralization, which is considered to be Late Precambrian crust. Its melting could have been caused by collisional processes, which began in the region in the Late Devonian–Early Carboniferous (Puchkov, 2010; Samygin and Burtman, 2009). In turn, there is no isotopic evidence of a significant contribution of juvenile mantle material.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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