

# Lead Isotope Characteristics of the Mindyak Gold Deposit, Southern Urals: Evidence for the Source of Metals

A.V. Chugaev<sup>a, \*</sup> and S. E. Znamensky<sup>b</sup>

<sup>a</sup>*Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, Moscow, 119017 Russia*

<sup>b</sup>*Institute of Geology, Ufa Scientific Center, Russian Academy of Sciences, Ufa, 450077 Russia*

\*e-mail: chug@igem.ru

Received August 18, 2016

**Abstract**—The isotopic composition of Pb in pyrite of the Mindyak orogenic gold deposit located in the Main Ural Fault Zone, the Southern Urals, has been studied by the high-precision MC-ICP-MS method. Orebodies at the deposit are composed of early pyrite and late polysulfide–carbonate–quartz mineral assemblages. The orebodies are localized in olistostrome with carbonaceous clayey-cherty cement. Pyrites from early and late mineral assemblages are close in Pb isotope ratios. For early pyrite  $^{206}\text{Pb}/^{204}\text{Pb} = 18.250\text{--}18.336$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.645\text{--}15.653$ ,  $^{208}\text{Pb}/^{204}\text{Pb} = 38.179\text{--}38.461$ ; while for late pyrite  $^{206}\text{Pb}/^{204}\text{Pb} = 18.102\text{--}18.378$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.635\text{--}15.646$ ,  $^{208}\text{Pb}/^{204}\text{Pb} = 38.149\text{--}38.320$ . The model parameters  $\mu_2$  ( $^{238}\text{U}/^{204}\text{Pb} = 9.91 \pm 2$ ),  $\omega_2$  ( $^{232}\text{Th}/^{204}\text{Pb} = 38.5 \pm 4$ ), and  $^{232}\text{Th}/^{238}\text{U} = 3.88 \pm 3$  indicate that an upper crustal Pb source played a leading role in ore formation. Carbonaceous shale as an olistostrome cement and syngenetic sulfide mineralization are considered to be the main Pb sources of both early and late mineral assemblages. An additional receipt in apparently magmatic lead is suggested for the late veinlet mineralization. The involvement of lead from several sources in ore formation is consistent with the genetic model, which assumes a two-stage formation of orebodies at the Mindyak deposit.

**Keywords:** lead isotopic composition, orogenic gold deposit, genesis, Mindyak deposit, Southern Urals

**DOI:** 10.1134/S1075701518010026

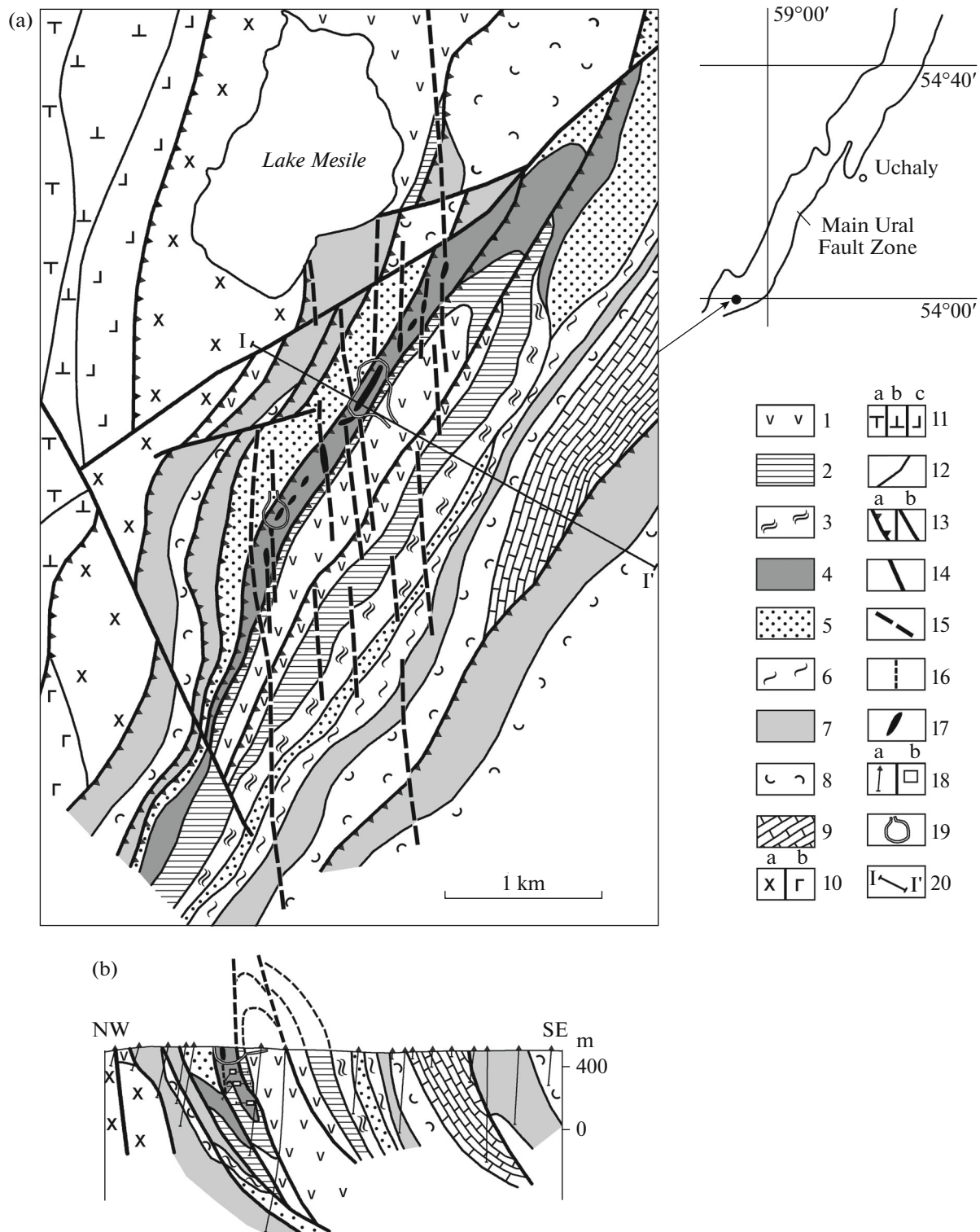
## INTRODUCTION

The Mindyak deposit is situated at northern end of the Magnitogorsk Megazone in the Southern Urals within the Main Ural Fault (MUFZ) 70 km southwest of the city of Uchaly in the Republic of Bashkortostan (Fig. 1). This is an orogenic deposit localized in black shale. Genesis of gold deposits belonging to this type is one of the controversial problems in contemporary ore geology. Hydrothermal–sedimentary, metamorphic, magmatic, polygenetic, and other models of their formation have been elaborated (Groves et al., 1998; Kerich et al., 2000; Bortnikov, 2006; Goryachev et al., 2008). At present, the metamorphic and polygenetic models are the most popular. According to the former, the ore components, including gold, are recovered from host rocks by fluids that originated owing to dehydration and decarbonation during regional metamorphism or were supplied to the ore-forming system from zones of high-temperature amphibolite-facies metamorphism (Buryak and Bakulin, 1998; Groves et al., 1998). According to (Morelli et al., 2007), mantle-derived fluids also participated in these processes. In terms of the polygenetic model, ore formation is related to tectono-magmatic activation, which supplies components separated from magma sources and

arising via dehydration and decarbonation due to contact or regional metamorphism (Bortnikov, 2006; Goryachev et al., 2008; Chernyshev et al., 2009). It is thought that preparation plays an important role, when host rocks possess noble-metal geochemical specialization (Rundqvist, 1997). Despite the long history of research, the genesis of gold mineralization for the Mindyak deposit remains debatable.

The Southern Ural segment of the MUFZ contains numerous orogenic gold deposits, mainly minor, which are hosted in Ordovician–Lower Carboniferous carbonaceous rocks subjected to Late Paleozoic collision and greenschist-facies metamorphism. Gold mineralization hosted in carbonaceous sequences deformed during two main stages of tectonic deformation that developed in the MUFZ of the Southern Urals during the Late Paleozoic general collision stage: (1) early thrusting and (2) the late strike-slip faulting in a general transpression regime (Znamensky et al., 2015). The deposits are poorly studied. The Mindyak deposit, with medium reserves, formed at the second stage under conditions of strike-slip dislocations.

The development of geological genetic models and, from them, the advanced development of fore-



**Fig. 1.** Schematic geological map (a) and section (b) of Mindyak deposit (Znamensky and Michurin, 2013). (1–9) tectonic sheets, bottom-up: (1) volcanic rocks ( $D_{2e1}$ ); (2) carbonate olistostrome ( $C_{1t-v}$ ); (3) melange of ultramafic rocks and gabbro; (4) ore-bearing polymictic olistostrome with carbonaceous clayey–cherty cement ( $C_{1s1}$ ); (5) terrigenous–carbonate rocks ( $D_3-C_1$ ); (6) melange of ultramafic rocks and gabbro; (7) carbonate olistostrome ( $C_{1v}$ ); (8) volcanic–sedimentary and cherty rocks ( $D_3$ ); (9) limestone ( $C_{1s1}$ ); (10) diorite and gabbro; (11) Mindyak ultramafic massif: (a) harzburgite–lherzolite series; (b) dunite–pyroxenite complex; (c) gabbro; (12) boundaries of tectonic sheets and rocks; (13) reverse-thrust faults dipping to southeast in plan view (a) and in section (b); (14) transfer fault; (15) secondary strike-slip fault in near-meridional tectonic zone; (16) ore-bearing fault in section; (17) orebody; (18) projection of borehole (a) and mining work (b); (19) contour of open pit; (20) line of geological section.

casting and prospecting of orogenic gold deposits hosted in carbonaceous complexes are urgent problems related to prospecting for gold over the last decade in the Southern Urals, including the MUFZ, which has been funded by Federal Agency for Subsurface Management. As is known, the sources of mineral-forming fluids and ore components are significant elements of these models.

In order to elucidate possible sources of material participating in ore formation at the Mindyak deposit, we have studied the Pb-Pb characteristics of ore pyrite. An isotopic study of lead at the gold deposit in the MUFZ in the Southern Urals was carried out for the first time.

#### BRIEF GEOLOGICAL CHARACTERIZATION OF THE DEPOSIT

The geological and structural position of the Mindyak deposit in the MUFZ has been determined by the intersection of two collisional faults: a NE-trending reverse–thrust fault and an overlapping zone of near-meridional low-amplitude strike-slip and oblique faults (Fig. 1). Within the deposit, the reverse–thrust fault consists of the system of imbricated W-trending segments complicating the northwestern limb of the antiform. The fold and imbricated faults are constrained along the strike by NE-trending (in the north) and NW-trending (in the south) transfer strike-slip faults. The packet of tectonic sheets is folded into an antiform. From bottom to top, these sheets are composed of (1) volcanic rocks ( $D_2e_1$ ), (2) carbonate olistostrome ( $C_1t-v$ ), (3) melange of ultramafic rocks and gabbro; (4) polymictic olistostrome ( $C_1s_1$ ); (5) terrigenous–carbonate rocks ( $D_3-C_1$ ), (6) melange of ultramafic rocks and gabbro, (7) carbonate olistostrome ( $C_1v$ ), (8) volcanic–sedimentary and cherty rocks ( $D_3$ ), and (9) limestone ( $C_1s_1$ ).

The formation of the packet of tectonic sheets, its subsequent folding into an antiform, and the development of second-generation imbricated reverse–thrust faults on the fold's limb took place at the first stage of Late Paleozoic deformations.

The main ore-bearing structure of the deposit is the right-lateral strike-slip fault zone that arose at the second stage of collisional deformation in the northwestern limb of the antiform at the spot of a steeply dipping reverse–thrust sheet. In its frame, the arrangement of mineralization was controlled by secondary faults, the kinematics and position of which correspond to Y-, R-, and R'-shears. The orebodies, which are complex in morphology, combine (i) early stringer–disseminated pyrite and (ii) late veinlet polysulfide (pyrite–chalcopyrite–sphalerite–galena) mineralization with native gold. The faults controlling the early and late ore assemblages formed in similar tectonophysical settings, which are characterized by stress fields of strike-slip and reverse–strike-slip types

and by a nearly latitudinal direction of stress (Znamensky et al., 2009), but under different thermodynamic conditions and, probably, as some researchers suggest (*Zolotonosnost Urala ...*, 2005), during different tectono-magmatic stages. This is reflected in the morphological features of ore-bearing faults. The stringer–disseminated pyrite ores are localized mainly in schistosity zones, where the host rocks were transformed into carbonate–albite–chlorite–sericite metasomatic rocks (Znamensky, 2009). The  $P$ - $T$ -parameters of ore formation ( $T = 340–450^\circ\text{C}$  and  $P = 0.50–0.66$  kbar) (Murzin et al., 2003) correspond to the thermodynamic conditions of the mesozone. The late mineralization is confined to minor brittle faults (breccia zones, tensile cracks, shear zones consisting of en echelon tensile cracks, etc.) and formed at  $T = 195–205^\circ\text{C}$  and  $P = 0.04–0.13$  kbar (Murzin et al., 2003), i.e., under virtually hydrostatic pressure (thermodynamic conditions of epizone). The wall-rock alteration is represented by sericite–carbonate–quartz metasomatic rocks. It should be noted that at the pre-ore stage, rocks of the deposit first underwent greenschist metamorphism and then listvenitization along fault zones.

The lithologic control of orebodies is distinctly expressed at the deposit. They are clustered in a sheet of polymictic olistostrome consisting of olistoliths and olistoplaques from a few tens to a few hundreds of meters in size and are composed of rocks of the ophiolitic association, limestone, carbonate breccia with Visian–Early Serpukhovian foraminifers, sandstone, and chert, probably Late Devonian age. The ophiolitic association is represented by serpentinite pyroxenites, hornblende gabbro, and dolerite close in chemistry to oceanic basalts of the Middle Ordovician Polyakovka Formation. The matrix is composed of strongly deformed carbonaceous clayey-cherty shales. The cement contains a large amount of syngenetic sulfides represented by fine disseminations of globular pyrite and larger pyrite nodules. The isotopic composition of sulfur in syngenetic pyrite is variable:  $\delta^{34}\text{S}$  ranges from  $-25.3$  to  $-5.2\%$  (Znamensky and Michurin, 2013). These data allow us to suggest sedimentary–biogenic origin of pyrite and to corroborate its syngenetic formation with respect to the host carbonaceous shales.

The ore-bearing olistostrome formed in a paleobasin localized in frontal part of a large thrust fault (Znamensky, 2009) at the stage of early (soft) collision of the Magnitogorsk island arc with the margin of the East European Platform ( $D_3-C_1$ ) (Puchkov, 2000; Herrington et al., 2005). The results of studying the S, C, O, and H isotopic compositions in minerals from the orebodies indicate the magmatic origin of the ore-forming fluids (Murzin et al., 2003; Znamensky and Michurin, 2013), the source of which remains unknown. At the same time, the close spectra of the REE distribution in ore pyrite and wall-rock metasomatic rocks, on the one hand, and in black shale and

syngenetic pyrite, on the other hand, allow us to suggest the participation of metamorphic components in ore formation (Znamensky and Michurin, 2013).

The isotopic age of gold mineralization has not been determined. According to geological data, it formed in the Late Paleozoic.

## RESEARCH METHODS

A Pb-Pb study of pyrite from ore of the Mindyak deposit was performed at the Laboratory of Isotopic Geochemistry and Geochronology, Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Science (RAS), by the MC-ICP-MS method. The chemical preparation of pyrite consisted in dissolution of 0.03–0.06 g samples in a 3 : 1 ratio of concentrated HNO<sub>3</sub> + HCl acids and subsequent separation of Pb by ion-exchange chromatography. Lead is separated from the elements of the matrix in an HBr medium on a chromatographic microcolumn (0.1 cm<sup>3</sup>) filled with anionite AG-1X8 (Chugaev et al., 2013). The total procedure blank does not exceed 0.15 ng.

The isotope ratios were measured on a NEPTUNE multicollector mass spectrometer (ThermoFinnigan, Germany) in the wet plasma regime. Immediately before isotopic analysis, thallium was introduced in the working solutions as a spike. In the course of analysis, the results of current measurements of Pb isotope ratios were corrected to the mass-bias at <sup>205</sup>Tl/<sup>203</sup>Tl = 2.3889 ± 1 spike. The uncertainty (±2SD) in measuring the Pb isotope ratios in pyrite did not exceed ±0.03% (Chernyshev et al., 2007; Chugaev et al., 2013).

The Pb, Th, and U contents in minerals were determined in the same sample aliquots as the Pb isotopic composition. The measurements were carried out on an X-7 ICP-MS quadrupole mass spectrometer (Thermo Elemental, United States) in solutions of samples traced with indium. The uncertainty of the Pb, Th, and U contents in mineral samples estimated from the results of systematic analyses of the international rock standards BHVO-2 and AGV-2 did not exceed ±3%. The obtained data on the Pb, U, and Th concentrations in the studied minerals were used to calculate the initial Pb isotope ratios.

## RESULTS AND DISCUSSION

The Pb isotopic composition in the gold mineralization at the Mindyak deposit was studied on 13 monomineralic fractions of pyrite. Six samples represented early stringer–disseminated ore, and the other seven, late polysulfide–carbonate–quartz ore. In addition, Pb-Pb data were obtained for a pyrite nodule taken from olistostrome cement beyond the boundaries of the ore zones. The analytical results are summarized in Table 1.

The isotopic composition of Pb in the gold mineralization is very heterogeneous for the contents of the radiogenic isotopes. The maximum variations of the measured values were established for ratios <sup>206</sup>Pb/<sup>204</sup>Pb (18.10–18.38) and <sup>208</sup>Pb/<sup>204</sup>Pb (38.15–38.46). Its scale can be estimated by the variation coefficient (*V*, %). Scattering of <sup>206</sup>Pb/<sup>204</sup>Pb (*V*<sub>6/4</sub> = 0.44%) and <sup>208</sup>Pb/<sup>204</sup>Pb (*V*<sub>8/4</sub> = 0.24%) exceeds the analytical uncertainty (±0.03%) by almost an order of magnitude and is thus geochemically significant. In contrast, the <sup>207</sup>Pb/<sup>204</sup>Pb ratios vary in a much more narrowly (from 15.635 to 15.653), and their range (*V*<sub>7/4</sub> = 0.03%) is comparable to the precision of the MC-ICP-MS method.

One of the geochemical causes of the revealed variations of the Pb isotopic compositions in pyrite is the presence in this mineral of a variable radiogenic addition of <sup>206</sup>Pb and <sup>208</sup>Pb, which was accumulated in situ after its crystallization. In addition to the geological age of the deposit, this is indicated by the results of measuring the U/Pb and Th/Pb ratios in the samples, the values of which vary in a wide range and reach 0.015 and 0.085, respectively. The elevated U and Th contents established in pyrite from the Mindyak deposit are, in general, characteristic of this mineral at gold ore objects localized in black shale (Chugaev et al., 2014). The elevated concentrations of these elements in pyrite are caused by inclusions of carbonic matter captured by the mineral when it was forming in metasedimentary rocks.

To correct the measured Pb isotope ratios to the existing radiogenic addition of <sup>206</sup>Pb and <sup>208</sup>Pb isotopes, the question of the age of gold mineralization at the deposit becomes of critical importance. The reasoning for the time of ore formation therein is mainly based on geological data. The lower age limit of mineralization is limited to the early Serpukhovian age of olistoliths and olistoplaques of limestone and lime breccia in ore-bearing olistostrome (327–323 Ma). The upper time boundary for ore at the Mindyak deposit is not reliable; however, taking into account the available Rb–Sr datings (295–255 Ma) for metasomatic wall rocks at other gold deposits in the northern part of the Magnitogorsk Megazone, including the MUFZ, which formed like they did at the Mindyak deposit at the Late Paleozoic stage of strike-slip faulting in a general transpression regime, 255 Ma can be accepted as the upper boundary (Znamensky and Znamenskaya, 2016).

The measured values of the Pb isotope ratios in pyrite have been corrected to the radiogenic addition, based on the Late Paleozoic (~300 Ma) age of the deposit. It should be noted that the existing uncertainty in estimating the ore formation time at the Mindyak deposit, which is ±40 Ma (see above), does not increase the total error in calculating the initial Pb isotope ratios for most of the studied samples. In this case, it is primarily determined by the analytical error

**Table 1.** Pb isotopic composition in pyrite of ore at Mindyak deposit and in pyrite nodule in host rocks

Sample	Pb, µg/g	Th, µg/g	U, µg/g	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
<b>Ore mineralization</b>						
<i>Pyrite of early mineral assemblage</i>						
B-171-1	94	0.93	0.34	18.2739	15.6452	38.2823
B-171-3	158	1.3	0.95	18.2921	15.6464	38.2925
B-171-4	229	2.1	0.59	18.2499	15.6517	38.1791
B-171-8	27	2.3	0.40	18.3352	15.6526	38.4607
B-171-15	43	2.1	0.29	18.3146	15.6489	38.3726
Yu-4-2	65	2.3	0.32	18.3357	15.6462	38.4074
<i>Pyrite of late mineral assemblage</i>						
B-171-13	480	2.5	0.25	18.1016	15.6380	38.1495
B-171-14	201	2.2	0.31	18.2572	15.6397	38.2315
B-171-16	170	5.2	0.66	18.1648	15.6349	38.1926
Yu-8	83	0.06	0.05	18.3048	15.6424	38.2735
3/2	331	0.06	0.15	18.3784	15.6464	38.3202
33/2	74	1.0	0.21	18.3774	15.6444	38.3131
K-91-1	245	3.3	0.41	18.2315	15.6416	38.2120
<i>Metamorphic and metasomatically altered pyrite (nodule)</i>						
K-11-3	28	0.03	0.07	18.3550	15.6548	38.2585

Pb, Th, and U contents determined in studied fractions of minerals using MC-ICP-MS method on a NEPTUNE mass spectrometer at Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM RAS). Uncertainty of Pb isotope ratios is  $\pm 0.03\%$  ( $\pm 2\text{SD}$ ).

( $\pm 0.03\%$ ), except for sample B-171-8, where the total error in estimating the initial  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratio proved somewhat higher than the error of analysis,  $\pm 0.04\%$ .

The correction of the Pb isotope ratios to radiogenic addition shows that the main geochemical cause of their variations is the primary heterogeneity of the Pb isotopic composition in the mineral-forming system of the deposit. The range of corrected  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios in pyrite of the mineralization is  $V_{6/4} = 0.42\%$  and  $V_{8/4} = 0.19\%$ , respectively. In terms of the scale of the established variations, the Mindyak deposit is related to the objects with heterogeneous Pb isotopic composition. This is characteristic of gold ore objects localized in metasedimentary rocks, e.g., for deposits of the Chertovo Koryto (Devil Trough) with  $V_{6/4} = 1.1\%$  and  $V_{8/4} = 0.6\%$ , Sukhoi Log ( $V_{6/4} = 0.9\%$  and  $V_{8/4} = 0.3\%$ ), and Verninsky ( $V_{6/4} = 0.7\%$  and  $V_{8/4} = 0.4\%$ ) (Chernyshev et al., 2009; Chugaev et al., 2010, 2014).

Comparison of the Pb-Pb data obtained for pyrites from early and late mineral assemblages reveals no statistically significant differences between them in the Pb isotopic compositions. For example, the calculated mean values of the Pb isotope ratios for pyrite of the early assemblage ( $^{206}\text{Pb}/^{204}\text{Pb}_{\text{av}} = 18.275 \pm 0.026$ ;  $^{207}\text{Pb}/^{204}\text{Pb}_{\text{av}} = 15.647 \pm 0.003$ ;  $^{208}\text{Pb}/^{204}\text{Pb}_{\text{av}} = 38.296 \pm 0.074$ ) coincide within the statistical scatter

( $\pm \sigma_{\text{av}}$ ) with those for pyrite of the late assemblage ( $^{206}\text{Pb}/^{204}\text{Pb}_{\text{av}} = 18.253 \pm 0.105$ ;  $^{207}\text{Pb}/^{204}\text{Pb}_{\text{av}} = 15.641 \pm 0.004$ ;  $^{208}\text{Pb}/^{204}\text{Pb}_{\text{av}} = 38.233 \pm 0.066$ ). At the same time, the substantially wider (four times) range of  $^{206}\text{Pb}/^{204}\text{Pb}$  for pyrite from the late mineralization is a distinguishing feature of the Pb-Pb data. The scales of variations for the other two isotope ratios  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  for pyrites of the early and late assemblages were similar.

The established similarity of the Pb isotopic compositions of pyrites from the early and late mineralization provides evidence for a common geochemical type of source of the ore lead. According to the obtained model parameter estimates, this source was characterized by a high U/Pb ratio ( $\mu_2 = ^{238}\text{U}/^{204}\text{Pb} = 9.91 \pm 0.02$ ), as well as an elevated Th/Pb ratio relative to the mean crustal ( $\omega_2 = ^{232}\text{Th}/^{204}\text{Pb} = 38.5 \pm 0.4$ ) and (Th/U =  $3.88 \pm 3$ ) ratios. The given Pb-Pb isotopic characteristics indicate that the evolution of ore lead took place in a crustal source before this element was concentrated in ore at the Mindyak deposit. The estimated time of ore lead separation from its source shows that the Pb-Pb model ages ( $t_m$ ) do not match the geological age of the deposit (C-P). The obtained time of  $t_m = 360 \pm 50$  Ma is in general older than the apparent geological age of the deposit. Since the estimated time of separation is based on the relationship

of uranium-generating  $^{206}\text{Pb}$  and  $^{207}\text{Pb}$  isotopes, the established divergence between  $t_m$  and the age of the deposit most likely shows a change (decrease) in the U/Pb ratio in the source with the evolution of the Pb isotopic composition. The character of this change may have resulted from the preore metamorphic and metasomatic processes that caused the partial removal of uranium, and as consequence, a drop in the U/Pb ratio. The elevated Th/U ratio in the source is evidence for this. In turn, the relatively small difference between  $t_m$  and the age of the deposit indicates that metamorphic and metasomatic transformations took place not long before ore formation.

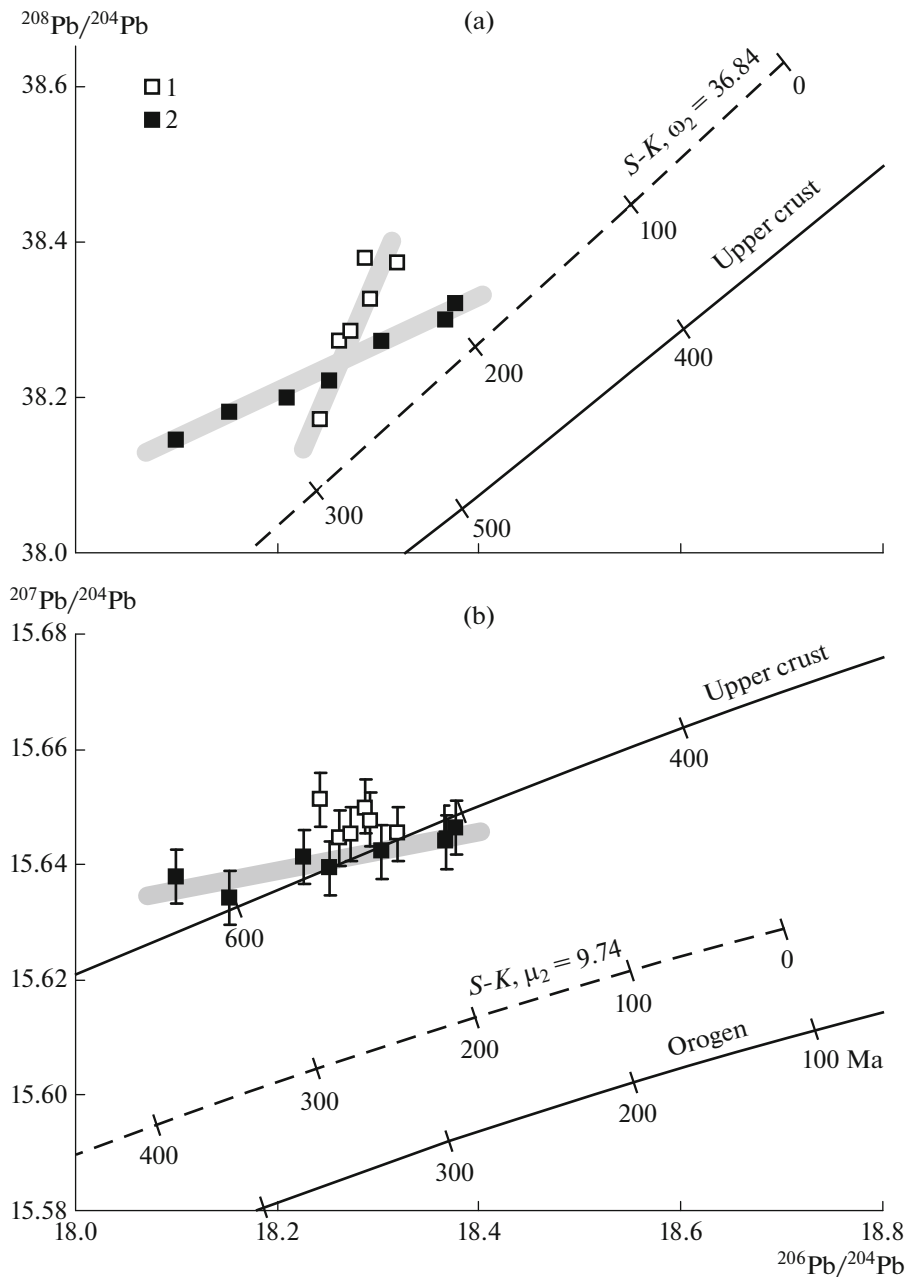
In order to identify the geochemical type of the source that supplied ore lead during the formation of gold mineralization at the Mindyak deposit, the obtained data were plotted in Pb-Pb diagrams (Figs. 2a, 2b). The evolutionary curves of Pb isotopes corresponding to the geochemical settings of the upper crust and orogenic domains according to the model of (Zartman and Doe, 1981), as well as the middle crustal evolutionary curve of the model of (Stacey and Kramers, 1975), are plotted in the same diagrams. The experimental points of the Pb isotopic composition of pyrite related to ore mineralization make up a compact field located close to the evolutionary curve of the Pb isotopic composition for the upper crustal source. In contrast to the plot with the uranium-generating  $^{206}\text{Pb}$  and  $^{207}\text{Pb}$  isotopes, in the plot where the  $^{208}\text{Pb}/^{204}\text{Pb}$  ratio is used as one of the coordinate axes (Fig. 2a), the field of ore Pb isotopic compositions from the Mindyak deposit is shifted with respect to the evolution curve of the upper and middle crust toward the domain of lower-crustal lead sources. As a rule, the points of ore lead isotopic compositions are located in this domain. Metamorphic rocks of the continental crust are their sources.

It should be noted that a number of differences in the disposition of pyrite points related to the early and the late mineral assemblages are revealed in both Pb-Pb plots. In the plot with the uranium-generating Pb isotopes, the pyrite points of the early assemblage make up a compact field, whereas the pyrite points of the late assemblage are clustered in a short linear trend, partly overlapped by the compact field. The differences are very contrasting in  $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{208}\text{Pb}/^{204}\text{Pb}$  coordinates, where pyrite points belonging to different mineral assemblages make up two mutually intersecting trends. The aforementioned disposition of pyrite points related to the early assemblage favors one lead source is similar in U–Th–Pb characteristics with the upper crustal source. This source, being relatively homogeneous in terms of the U/Pb ratio, remains heterogeneous in terms of the Th/Pb and Th/U ratios, as follows from the  $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{208}\text{Pb}/^{204}\text{Pb}$  trend for pyrite of the early assemblage. In turn, for pyrite of the late assemblage, the trends in both plots can be interpreted as lines of Pb mixing. In this case, they reflect

mixing of lead differing in isotopic compositions supplied to the mineral-forming system of the deposit from two sources, as a minimum. One of them is similar in the U–Th–Pb isotopic–geochemical features to the source of lead of the early mineralization. Consideration of obtained Pb-Pb data allows the conclusion that in the formation of the early and late mineral assemblages, the lead role is played by ore from a Pb source of the upper crustal type. However, the formation of the late mineralization requires an additional gain of lead from another source, although its contribution to the lead supply to the fluid was insignificant.

The aforementioned common geochemical characteristics of the ore lead that participated in the formation of the gold mineralization at the Mindyak deposit, indicates that this source is most likely composed of rocks that formed in the upper crustal setting. In order to identify possible sources of ore Pb, we studied the Pb-Pb isotopic characteristics of widespread metasedimentary rocks near the deposit. The isotopic composition of Pb was measured in metamorphosed and hydrothermally altered pyrite from a nodule taken from a barren unit of carbonaceous shale and chert (Table 1). The obtained Pb-Pb data on both the pyrite nodule and pyrite from ore at the deposit are compared in Fig. 3. The Pb-Pb data on metagabbroic rocks of the Mindyak massif in (Spadea and D'Antonio, 2006) are given in Fig. 3 as well. The isotopic  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  ratios for the pyrite nodule and metagabbroic rocks are recalculated to the suggested age of the deposit (300 Ma). In the plot, an experimental point corresponding to the pyrite nodule is located near the field of the Pb isotopic composition for pyrite from the gold mineralization at the Mindyak deposit. The recorded relationship between the isotopic compositions of Pb in the pyrite from the nodule and from the orebody provides evidence that metasedimentary rocks were a probable source of metals supplied in the ore-forming system of the deposit. This conclusion is corroborated by close REE distribution patterns in carbonaceous shale, syngenetic pyrite mineralization, and ore pyrite. In turn, the Pb isotopic composition in metagabbro of the Mindyak massif differing by much lower concentrations of radiogenic  $^{206}\text{Pb}$  and  $^{207}\text{Pb}$  isotopes compared with Pb in pyrite of the mineralization rules them out as a potential source of ore Pb.

Taking into account the possibility of Pb supply from one source, for which we understand the host metasedimentary rocks at various stages of ore formation at the Mindyak deposit, we can explain the known differences in the variation of the Pb isotopic composition in pyrite of the early and late mineral assemblages, in particular, the disposition of pyrite points of the late assemblage in the  $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{207}\text{Pb}/^{204}\text{Pb}$  plot, which form the upper part of the trend, to the right of the field of the Pb isotopic composition in pyrite of the early mineral assemblages. The observ-



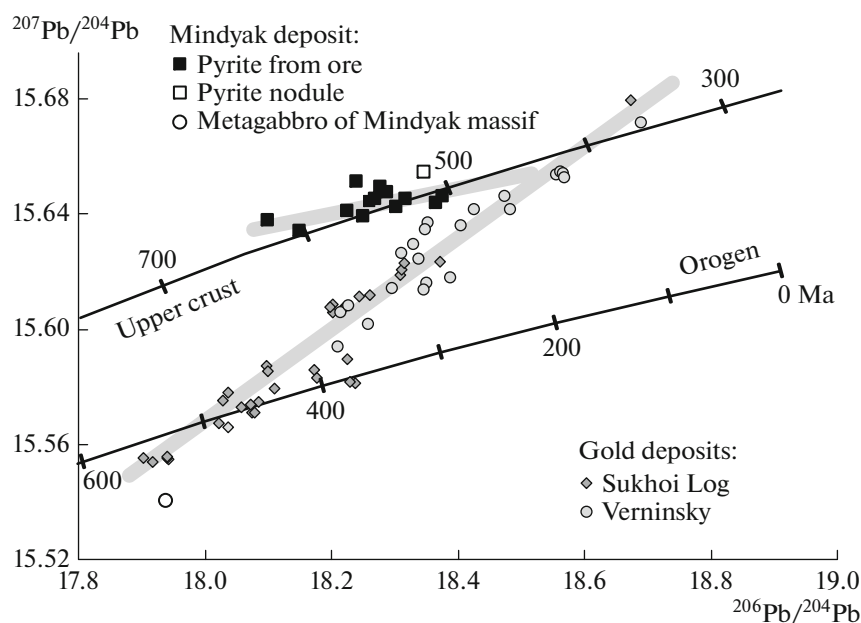
**Fig. 2.** Pb-Pb plots of pyrite from mineralization at Mindyak deposit. Pyrite: 1 – early stringer–disseminated mineralization; 2 – late veinlet mineralization. Graph in coordinates of  $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{207}\text{Pb}/^{204}\text{Pb}$  for experimental points shows uncertainty ( $\pm 0.03\%$ ) of measured  $^{207}\text{Pb}/^{204}\text{Pb}$  ratio. For two other Pb isotope ratios uncertainty is less than symbol or commensurable with dimension of latter. Solid and dash lines correspond to evolutionary curves of Pb isotopic composition in various geochemical reservoirs according to models of (Stacey and Kramers, 1975) and (Zartman and Doe, 1981), respectively. Trends of lead isotopic composition in pyrite from various mineral assemblages in ores at Mindyak deposit are marked in gray.

able relationship may indicate a gain in the radiogenic isotope  $^{206}\text{Pb}$  in the upper crustal source over the period of time separating the early and late assemblages at the deposit. Accepting this model, we estimated the possible duration of this temporal period.

The following values of the initial parameters were used in model calculations. Because the points of the Pb

isotopic composition in pyrite from the ore assemblage at the Mindyak deposit are located near the upper crustal evolutionary curve of the model of (Zartman and Doe, 1981), a value equal to that in source of this type is accepted for parameter  $\mu$  ( $\mu = 13.22$ ). In estimating the  $\Delta^{206}\text{Pb}/^{204}\text{Pb}$  value, which characterizes a change in the content of the isotope  $^{206}\text{Pb}$  in the source





**Fig. 3.** Pb-Pb plot for pyrite from orebodies at Mindyak deposit and pyrite nodule from host black shale, as well as for metagabbro of Mindyak ultramafic massif according to data of (Spadea and D'Antonio, 2006). Graph also shows Pb-Pb data for Verninsky and Sukhoi Log gold deposits (Chernyshev et al., 2009; Chugaev et al., 2014).

between ore formation stages, the initial  $^{206}\text{Pb}/^{204}\text{Pb}$  value is taken as 18.300. This value is the mean for pyrite from the early assemblage, so that only one source of Pb is established. In contrast, the involvement of two sources is inferred for ore formation for the late assemblage. One of them, which contains a higher radiogenic Pb isotope composition, is brought into correlation with the host metasedimentary rocks. Hence, it follows that the maximum value  $(^{206}\text{Pb}/^{204}\text{Pb})_{t=300} = 18.377$  obtained for late pyrite will be closest to that in the source at the moment of formation of the late ore assemblage.

The calculations show that the time interval dividing the early and late ore assemblages can be measured in the first tens of millions of years (~40 Ma). This estimate looks quite realistic, taking into account the aforementioned geochronological data on other gold deposits at the northern closure of the Magnitogorsk Megazone. They are clustered into two discrete age groups, the early one of which combines gold-sulfide deposits with the Rb-Sr isochron ages of 295 Ma (Murtykty) and 288 Ma (Karagaily), and late group of gold-sulfide-quartz deposits and occurrences with Rb-Sr ages of 266 Ma (Minor Karan) and 255 Ma (Rytovsky Veins) (Znamensky and Znamenskaya, 2016).

In discussing on source material, it is of a certain interest to compare the available Pb-Pb data on the Mindyak deposit with the results of similar lead isotopic studies of other gold objects spatially and genetically related to black shale. As objects of comparison, we chose two large gold deposits in Russia—Sukhoi

Log and Verninsky—which are situated in the northeastern Transbaikalian metallogenic provinces within the Bodaibo Synclinorium. Detailed Pb-Pb data were also obtained by the high-precision MC-ICP-MS method (Chernyshev et al., 2009; Chugaev et al., 2014). The disseminated and quartz-vein mineralization of the Sukhoi Log and Vernikovsky deposits are localized in Vendian terrigenous and carbonate rocks. The age of disseminated ore has been determined as Late Ordovician–Early Silurian ( $447 \pm 6$  Ma, Rb-Sr isochron method (Laverov et al., 2007)). Long-standing isotopic-geochemical studies of ore and gangue materials have shown that in the formation of these objects, the lead role was played by metasedimentary rocks as a source of material (Kryazhev et al., 2009; Chernyshev et al., 2009; Dubinina et al., 2010, 2014; Chugaev et al., 2014).

In the Pb-Pb plot, the points of the Pb isotopic composition of ore minerals from the Sukhoi Log and Verninsky deposits make up a single linear trend, which differs by the longer extent and steeper inclination from the trend of the Pb isotopic composition for the Mindyak deposit (Fig. 3). Both of the considered trends intersect near the evolutionary curve of lead for the geochemical reservoir of the upper crustal type, and this is evidence for the participation of this source in the genesis of these deposits. At the same time, there is a fundamental difference in the Pb-Pb characteristics of the Mindyak deposit, on the one hand, and the Sukhoi Log and Verninsky deposits, on the other. In the latter deposits, orogenic Pb participated in ore formation, whereas at the Mindyak deposit, this



geochemical type of source has not been established. It should be noted that the gold mineralization at deposits related to black shale, as a rule, inherited the Pb-Pb characteristics of host metasedimentary sequences. Therefore, the revealed difference in the Pb isotope composition between the Mindyak deposit and gold objects of the Bodaibo Synclinorium is primarily caused by the corresponding differences in the geochemical types of clastic material supplied to paleobasins. According to the available geodynamic reconstructions, the terrigenous-carbonate sequences that fill the Bodaibo Synclinorium initially formed in the marine paleobasin that originated on the thinned continental crust of the passive margin of the Siberian Craton (Kuz'min et al., 2006; Zorin et al., 2009; Nemerov et al., 2010). It has been suggested that terrigenous material primarily was supplied from the Siberian Craton, as a result of weathering of Archean and Paleoproterozoic crystalline rocks. However, at the late stage of evolution of the paleobasin, the aforementioned clastic material was supplemented by the scouring products of igneous rocks from Neoproterozoic island arcs (Zorin et al., 2009; Nemerov et al., 2010; Chugaev et al., 2017). Mixing of terrigenous material in the paleobasin and, correspondingly, of lead from two sources differing in U-Th-Pb characteristics led to significant initial heterogeneity of the Pb isotopic compositions in metasedimentary sequences of the Bodaibo Synclinorium and the occurrence of upper crustal and orogenic types of lead in ores at Sukhoi Log and Verninsky deposits. In contrast to the metasedimentary sequences of the Bodaibo Synclinorium, the ore-bearing olistostrome at the Mindyak deposit formed in the collisional geodynamic setting of the basin controlled by thrust faulting. The main source of terrigenous material in carbonaceous shale in olistostrome cement was likely rocks of accretionary Uraltau Zone. At the latitude of the Mindyak deposit, they are represented by Precambrian metamorphic complexes (Kozlov, 1988). The material of Uraltau metamorphic rocks has been established in Visian-Serpukhovichian sedimentary rocks in many segments of the MUFZ (Gorozhanina et al., 2009; Mizens, 2002).

## CONCLUSIONS

The Pb-Pb study of the Mindyak deposit allowed us to identify one of the potential sources of ore lead (probably of other metals as well) that participated in the genesis of gold mineralization. This source, which corresponds in its U-Th-Pb isotopic characteristics to a geochemical reservoir of the upper crustal type, is composed of carbonaceous clayey-cherty shale making up the cement of ore-bearing olistostrome, along with syngenetic sulfide mineralization. This conclusion agrees with the lithologic control of mineralization at the deposit. The carbonaceous shale was involved in mineral formation during early pyritic

stringer-disseminated ore formation and the late polysulfide (pyrite-chalcopyrite-sphalerite-galena)-carbonate-quartz mineral assemblage.

The formation of the late mineral assemblage is also characterized by additional gain of lead from another crustal source with a specific U-Th-Pb composition. The available Pb-Pb data do not directly confirm the participation of a magmatic source of metals in the formation of gold mineralization. Judging by the isotopic composition of S, C, O, and H in ore minerals, a granitic melt nevertheless might have been such a source. Therefore, it should be noted that the stage of Late Paleozoic strike-slip deformations was accompanied by the origin of minor intrusions, including dikes, at the northern closure of the Magnitogorsk Megazone (Znamensky, 2009). However, at the Mindyak deposit and in adjacent areas, they have not yet been established.

The revealed differences in sources of ore lead in the early and late mineral assemblages agree with the existing reasoning of the two-stage formation of orebodies at the Mindyak deposit. The Pb-Pb model estimates indicate that the time period separating these stages most likely did not exceed a few tens of millions of years.

## REFERENCES

- Bortnikov, N.S., Geochemistry and origin of the ore-forming fluids in hydrothermal-magmatic systems in tectonically active zones, *Geol. Ore Deposits*, 2006, vol. 48, no. 1, pp. 1–22.
- Buryak, V.A. and Bakulin, Yu.I., *Metallogeniya zolota* (Gold Metallogeny), Vladivostok: Dal'nauka, 1998.
- Chernyshev, I.V., Chugaev, A.V., and Shatagin, K.N., High-precision Pb isotope analysis by multicollector-ICP-Mass-spectrometry using  $^{205}\text{Tl}/^{203}\text{Tl}$  normalization: optimization and calibration of the method for the studies of Pb isotope variations, *Geochem. Int.*, 2007, vol. 45, no. 11, pp. 1065–1076.
- Chernyshev, I.V., Chugaev, A.V., Safonov, Yu.G., et al., Lead isotopic composition from data of high-precision MC-ICP-MS and sources of matter in the large-scale Sukhoi Log noble metal deposit, Russia, *Geol. Ore Deposits*, 2009, vol. 51, no. 6, pp. 496–504.
- Chugaev, A.V., Chernyshev, I.V., Safonov, Yu. G., and Saroyan, M. R., Rb-Sr isotopic systematic of hydrothermal minerals, age, and matter sources of the Nezhdaninskoe Gold Deposit (Yakutia), *Dokl. Earth Sci.*, 2010, vol. 434, pp. 1337–1341.
- Chugaev A.V., Chernyshev I. V., Lebedev V. A., Eremina A. V. Lead isotope composition and origin of the Quaternary lavas of Elbrus Volcano, the Greater Caucasus: high-precision MC-ICP-MS data, *Petrology*, 2013, vol. 21, no.1, pp. 16–27.
- Chugaev, A.V., Plotinskaya, O.Yu., Chernyshev, I.V., and Kotov, A.A., Lead isotope heterogeneity in sulfides from different assemblages at the Verninskoe Gold deposit (Baikal-Patom Highland, Russia), *Dokl. Earth Sci.*, 2014, vol. 457, pp. 887–892.
- Chugaev, A.V., Budyak, A.E., Chernyshev, I.V., et al., Sources of clastic material of the Neoproterozoic metased-

- imentary rocks of the Baikal–Patom Belt, Northern Transbaikalia: evidence from Sm–Nd isotope data, *Geochem. Int.*, 2017, vol. 55, no. 1, pp. 60–68.
- Dubinina, E.O., Ikonnikova, T.A., and Chugaev, A.V., Heterogeneity of the sulfur isotopic composition of pyrite at the Sukhoi Log Deposit, and its controlling factors, *Dokl. Earth Sci.*, 2010, vol. 435, pp. 1665–1669.
- Dubinina, E. O., Chugaev, A. V., Ikonnikova, T. A., et al., Sources and fluid regime of quartz–carbonate veins at the Sukhoi Log gold deposit, Baikal–Patom Highland, *Petrology*, 2014, vol. 22, no. 4, pp. 329–358.
- Gorozhanina, E.N., Pazukhin, V.N., and Gorozhanin, V.M., Paleofacies model of sedimentation of the Lower Carboniferous sediments on the South Urals, *Tipovye razrezy karbona Rossii i potentsial'nye global'nye stratotipy. Yuzhnoural'skaya sessiya: Materialy Mezhdunarodnogo polevogo soveshchaniya* (Type Sections of the Russian Carboniferous and Poyential Global Stratotypes. South Uralian Session. Proceedings of the International Field Conference), Ufa: DizainPoligrafServis, 2009, pp. 12–21.
- Goryachev, N.A., Vikent'eva, O.V., Bortnikov, N.S., Prokof'ev, V.Yu., Alpatov, V.A., and Golub, V.V., The world-class Natalka gold deposit, Northeast Russia: REE patterns, fluid inclusions, stable oxygen isotopes, and formation conditions of ore, *Geol. Ore Deposits*, 2008, vol. 50, no. 5, pp. 362–390.
- Groves, D.I., Goldfarb, R.J., Gebre-Mariam, M., et al., Orogenic gold deposits: a proposed classification in the context of their crustal distribution and relationship to other gold deposit types, *Ore. Geol. Rev.*, 1998, vol. 13, pp. 7–27.
- Herrington, R.J., Zaykov, V.V., Maslennikov, V.V., et al., Mineral deposits of the Urals and links to geodynamic evolution, *Econ. Geol.*, 2005, vol. 100, pp. 1069–1095.
- Kerrick, R., Goldfarb, R.J., Groves, D.I., and Garwin, S., The geodynamics of word-class gold deposits: characteristics, space-time distribution and origins, *Rev. Econ. Geol.*, 2000, vol. 13, pp. 501–551.
- Kozlov, V.N., Main problems of the Upper Precambrian stratigraphy of the South Urals and eastern Russian Platform, in *Verkhniy dokembrii Yuzhnogo Urala i vostochno Russkoi platform* (Upper Precambrian of the South Urals and eastern Russian Platform), Ufa: BNTs UrO AN SSSR, 1988, pp. 4–9.
- Kryazhev, S. G., Ustinov, V. I., and Grinenko, V. A., Fluid Regime at the Sukhoi Log Gold Deposit: Isotopic Evidence, *Geochem. Int.*, 2009, vol. 47, no. 10, pp. 1041–1049.
- Kuz'min, M.I., Yarmolyuk V.V., Spiridonov, A.M., et al., Geodynamic setting of gold ore deposits of the Neoproterozoic Bodaibo Trough, *Dokl. Earth Sci.*, 2006, vol. 407, pp. 397–400.
- Laverov, N.P., Chernyshev, I.V., Chugaev, A.V., et al., Formation stages of the large-scale noble metal mineralization in the Sukhoi Log Deposit, East Siberia: results of isotope–geochronological study, *Dokl. Earth Sci.*, 2007, vol. 415, pp. 810–814.
- Mizens, G.A., *Sedimentatsionnye basseiny i geodinamicheskie obstanovki v pozdnem devone - rannei permi yuga Urala* (Late Devonian–Early Permian Sedimentation Basins and Geodynamic Settings of the South Urals), Yekaterinburg: IGGG UrO RAN, 2002. 190 s.
- Morelli, R., Creaser, R.A., Seltman, R., et al., Age and source constraints for giant Muruntau gold deposit, Uzbekistan, from coupled Re–Os–He isotopes in arsenopyrite, *Geology*, 2007, vol. 35, pp. 759–798.
- Murzin, V.V., Bortnikov, N.S., Sazonov, V.N., et al., Origin of ore-forming fluid at the Mindyak gold deposit, South Urals, *Evolutsiya vnutrikontinental'nykh podvizhnykh poyasov: tektonika, magmatizm, metamorfizm, sedimentogenez, poleznye iskopaemye: mater. nauch. konf. (IX Chteniya A.N. Zavaritskogo)* (Evolution of Intracontinental Mobile Belts: Tectonics, Magmatism, Megtamorphism, Sedimentogenesis, and Mineral Resources. Proceedings of the Scientific Conference, 9<sup>th</sup> Zavaritskii Reading), Yekaterinburg: IGG UrO RAN, 2003, pp. 197–199.
- Nemerov, V. K., Stanevich, A. M., Razvozzhaeva, E. A., et al., Biogenic sedimentation factors of ore formation in the Neoproterozoic strata of the Baikal–Patom region, *Russ. Geol. Geophys.*, 2010, vol. 51, no 5, pp. 572–586.
- Puchkov, V.N., *Paleogeodinamika Yuzhnogo i Srednego Urala* (Paleogeodynamics of the South and Middle Urals), Ufa: Dauriya, 2000.
- Rundqvist, D.V., Time factor in the formation of hydrothermal deposits: periods, epochs, megastages, and ore formation stages, *Geol. Rudn. Mestorozhd.*, 1997, vol. 39, no. 1, pp. 11–24.
- Spadea, P. and D'Antonio, M., Initiation and evolution of intra-oceanic subduction in the Uralides: geochemical and isotopic constraints from Devonian oceanic rocks of the Southern Urals, Russia, *Island Arc*, 2006, vol. 15, pp. 7–25.
- Stacey, J.S. and Kramers, I.D., Approximation of terrestrial lead isotope evolution by a two-stage model, *Earth Planet. Sci. Lett.*, 1975, vol. 26, no. 2, pp. 207–221.
- Zartman, R.E. and Doe, B., Plumbotectonics—the model, *Tectonophysics*, 1981, vol. 75, pp. 135–162.
- Znamenskii, S.E., *Strukturnye usloviya formirovaniya kollizionnykh mestorozhdenii zolota vostochnogo sklona Yuzhnogo Urala* (Structural Conditions of Formation of Collisional Gold Deposits on the Eastern Slope of the South Urals), Ufa: Gilem, 2009.
- Znamenskii, S. E. and Michurin, S. V., Conditions of formation of the Mindyak gold–sulfide deposit (South Urals): structural and isotope–geochemical aspects, *Litosfera*, 2013, no. 4, pp. 121–135.
- Znamenskii, S.E. and Znamenskaya, N.M., Structural control and prospects of searching gold mineralization in the Nurali–Voznesensk–Buidin Fault Zone, South Urals, *Georesursy*, 2016, vol. 18, no. 1, pp. 14–18.
- Znamenskii, S.E., Puchkov, V.N., and Michurin, S.V., Sources of ore-forming fluids and formation environments of orogenic Au deposits in the Main Uralian Fault Zone (Southern Urals), *Dokl. Earth Sci.*, 2015, vol. 464, pp. 910–913.
- Zolotonosnost' Urala. Ob'yasnitel'naya zapiska k karte korennoi zolotonosnosti Urala masshtaba 1 : 1000000* (Gold Potential of the Urals, Explanatory Notes to the Map of Bedrock Gold Potential of the Urals on a Scale 1 : 1000000), Krivtsov, A.I., Ed., Moscow: TsNIGRI, 2005.
- Zorin, Yu.A., Sklyarov, E.V., Belichenko, V.G., and Mazukabzov, A.M., Island-arc–back-arc basin evolution: implications for Late Riphean–Early Paleozoic geodynamic history of the Sayan–Baikal folded area, *Russ. Geol. Geophys.*, 2009, vol. 50, no. 3, pp. 149–161.

Translated by V. Popov