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Distribution of Indium in Ores of Some Base Metal and Tin–Sulfide Deposits in Siberia and the Russian Far East

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Abstract—The study of base-metal massive sulfide and tin–sulfide deposits in Siberia and the Russian Far East has revealed that the indium content in ores exceeding the average statistical value at similar deposits worldwide could be economically important. Sphalerite and chalcopyrite and bornite, and sphalerite are the major indium carriers in the base-metal massive sulfide and tin–sulfide ores, respectively. In addition, base-metal massive sulfide ores have high Cd, Ag, and Te contents, whereas tin–sulfide ores have elevated Ge, Ga, and Nb contents. This has stimulated the investment attractiveness of these deposits.

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INTRODUCTION

Indium is a typical rare and trace element. Despite its low mean global content in the Earth's crust ($1.4 \times 10^{-5}\%$), this metal is widely used in the modern high-tech industry. Indium is used in nuclear reactors, microelectronics, LED displays, astronomy, electrochemistry, and nuclear energy. In the world market, the demand for this metal is compared with explored reserves available for economic ore processing. According to the calculations of the Indium Corporation, in the upcoming decades, demand will double and indium production will be needed for the long term. Due to increasing demand for indium, already known ore districts, explored deposits, and tailings of mining processing plants in Siberia and Russian Far East should be evaluated in a new light as probable indium sources.

BRIEF REVIEW OF FOREIGN INDIUM DEPOSITS AND PROSPECTIVE RUSSIAN SOURCES

At present, base-metal (70–75%) and tin–sulfide (10–15%) deposits are the major indium producers. A high In content has been found at Freiberg silver–base-metal deposits in the Eastern Ore Mountains, Germany, among base-metal deposits proper. Here, sphalerite contains up to 0.38 wt % In (occasionally up

to 2.9 wt %). A high In content (75.83 ppm) was also found from base-metal deposits of the Lo Gam structure, Northeastern Vietnam (Tran Tuan Anh et al., 2012). Massive sulfide deposits (Gai, Uzelga, and Safyanovka) in which the indium content ranges from 10 to 24 ppm are the major indium producers in Russia. An elevated indium content was identified at the Sadon Pb–Zn deposits of the Sadon District in the North Caucasus (Sadon, Zgid, Arkhon, Kholst) (Khetagurov, 1973) and massive sulfide deposits of Ore Altai (Gaskov et al., 2005).

A high indium content is characteristic of complex tin–base-metal deposits. For example, the indium content in the ores of the Rio Tinto massive sulfide deposit largest over the Iberian belt characterized by the high Sn content (up to 37 wt % in some pockets) is 0.4 wt %. There, sphalerite contains up to 1.5 wt % In and 1 wt % Sn (Nehlig et al., 1998). Elevated indium contents within the Iberian belt were established at the Neves Corvo massive sulfide (with tin) and Lagoa Salgada base-metal massive sulfide deposits (Benzazoua et al., 2003; Arseneau, 2007). At the Neves Corvo deposit, the In content in massive Cu–Sn ores is 150–300 ppm; in some minerals, it ranges from 0.09 to 0.28 wt % in sphalerite, from 0.06 to 0.21 wt % in chalcopyrite, from 0.06 to 0.20 wt % in tennantite, and from 0.22 to 3.01 wt % in stannite (Schwarz-Schampera and Herzig, 2002). Pyrite and sphalerite, the most abun-

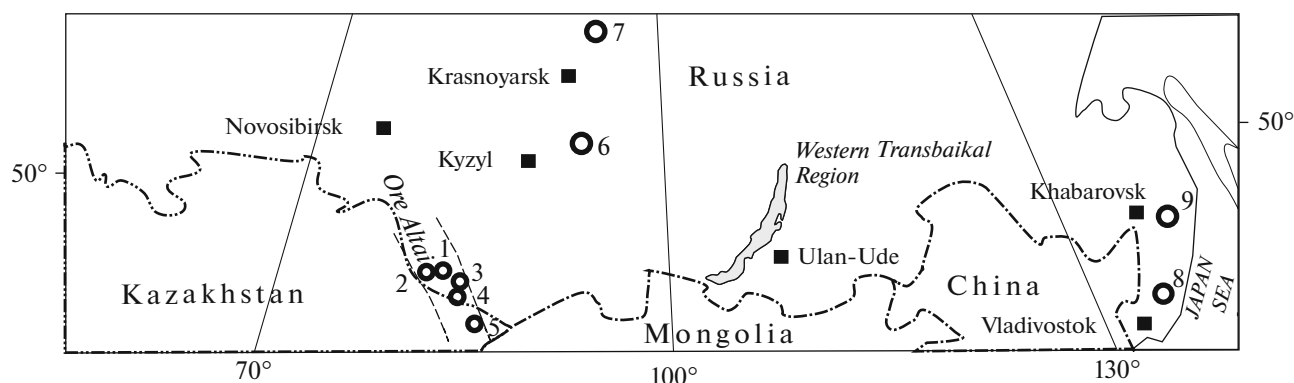


Fig. 1. Geographical location of (1–7) base metal and (8, 9) tin–sulfide deposits. (1) Zakharovskoe, (2) Yubileiny, (3) Karbalikha, (4) Zarechenskoe, (5) Maleev, (6) Kyzyl-Tashtyg, (7) Gorevsky, (8) Tigrinoe, (9) Pravoutmiisky.

dant minerals at the Lagoa Salgada deposit, contain 40–80 and 190–270 ppm In, respectively (Oliveira et al., 2009). High indium contents were established at tin–base-metal deposits in Japan (Toyoha, Ashio, Akenobe), China (Dulong, Dachang), and Bolivia (Potosi, Huari Huari, Bolivar, Porco) (Murakami and Ishihara, 2013) and in tin–base-metal deposits in Primorsky and Khabarovsk kraia, Russian Far East, where the In content reaches 1.5 wt % and 1300 ppm in sphalerite and chalcopyrite (Flerov et al., 1971; Geology, Mineralogy ..., 1971; Butova et al., 1998; Gavrilenko et al., 1992). Schwarz-Schampera and Herzig (2002) give more information on the indium content in ores of this type of deposits.

The aforesaid demonstrates that base-metal massive sulfide and tin–sulfide deposits in Siberia and Far East should be emphasized in Russia (Fig. 1). Preliminary study of these deposits unambiguously testifies to their promise for In, Cd, Ag, Te, Ge, Ga, Nb, and other valuable and high-demand trace elements (Gonevchuk, 2002; Gonevchuk et al., 2005; Pravourmiisky deposit, 2006; Popova et al., 2013; Pavlova et al., 2013, 2015; Gaskov et al., 2014; Gaskov and Vladimirov, 2014).

As judged by the indium content at the explored base-metal massive sulfide and tin–sulfide deposits, Siberia and the Russian Far East are world class indium metallogenic provinces in both reserves and ore grade (Schwarz-Schampera and Herzig, 2002; Pavlova et al., 2015). Data from other indium deposits can be provided for comparison: the Baal Gammon Ag–In Project (150 metric tons of indium) in Australia shows the average content of In in ore is 50 ppm and total ore reserves are 3 Mt (Schwarz-Schampera and Herzig, 2002). The Malku Khota (Bolivia, South America) Ag–Ga–In Project located 200 km north of the Potosi deposit in South America with possible reserves of indium and silver about 2 kt and 10 kt with average contents of 15 and 125 ppm, respectively, is the largest in recent years. The total indium reserves at tin–sulfide deposits in Bolivia (San Lorenzo, Bolivar,

Huari-Huari, Porco, Colquechaca, and Colquiri) are 12 kt with an average indium content of 15 ppm. In China, indium is produced from tin–sulfide ores of the Dachang District with an indium content ranging from 10 to 236 ppm (reserves not published).

AIM, METHODS, AND OBJECTS

This article reports the distribution of indium and accompanying trace elements (Ag, Cd, In, Sn, Sb, Te) in the ores of base-metal massive sulfide and base-metal deposits in Siberia (Yubeleiny, Korbalkha, Zakharovskoe, Maleev, and Zarechensky in Ore Altai, Kyzyl-Tashtyg in the Eastern Tyva, and Gorevsky in Enisey Ridge) and in tin–sulfide ore deposits in the Russian Far East (Tigrinoe and Pravourmiisky) (Fig. 1). Tailings of the Novosibirsk tin plant and Solnechny mining and processing works in the Komsomolsk ore district, Russian Far East, occupy a special place. Previous schemes for processing of tin–sulfide ores used in Russia focused on only tin recovery, whereas all other constituents including indium ran to waste. Therefore, economic reserves of rare metals were accumulated in tailings of processing plants, which could be regarded as technogenic deposits (Khanchuk et al., 2012).

The absence of modern analytical methods for determining the low indium content in both ores and ore minerals complicated the solution of this problem. At present, the Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences, Novosibirsk, proposed and tested at some deposits an express XRF technique with synchrotron radiation (SR-XRF), which allows reliable measurements at a level of 1–10 ppm In (Vladimirov et al., 2014).

BASE-METAL MASSIVE SULFIDE DEPOSITS

The group of base-metal massive sulfide deposits comprises deposits from various ore districts in Siberia with predominance of Ore Altai deposits of different

mineral types: Maleevskoe copper massive sulfide; Yubileiny, Korbalikha, and Zakharovskoe base-metal massive sulfide; and Zarechenskoe barite–base-metal. In addition, copper–zinc massive sulfide ores of the Kyzyl-Tashtyg deposit in Eastern Tyva and predominant lead ores of the Gorevsky in Enisei Ridge were studied.

The base-metal massive sulfide deposits of Ore Altai, which are closely related to the Middle to Upper Devonian basalt–rhyolite volcanic association, are located at various stratigraphic levels (Gaskov et al., 2005). At various deposits, predominantly sheetlike and lenticular stratified orebodies are hosted in volcanic sedimentary rocks (Figs. 2a–2d). The orebodies are accompanied by asymmetric halos of metasomatic quartz–sericite and sericite–quartz–chlorite rocks. Pocket–stringer–disseminated and massive ores are composed of fine-grained colloform and globular aggregates. All Ore Altai deposits belong to the volcanogenic base-metal massive sulfide assemblage, which is divided into several types: copper massive sulfide, base-metal massive sulfide proper, and barite–base-metal. Pyrite, sphalerite, galena, and chalcopyrite are the major minerals; fahlore, marcasite, pyrite, digenite, and altaite are minor. These are volcanogenic hydrothermal deposits and formed at a comparatively low temperature (200–350°C).

The Kyzyl-Tashtyg deposit in the Tyva Republic is a compact lenticular zoned lode hosted in a Lower Cambrian volcanic sedimentary sequence comprising intercalated dacite, basalt, their tuffs, and carbonaceous shales (Fig. 2e). The lower root zones are pocket–stringer and stringer–disseminated quartz–chalcopyrite–pyrite and pyrite ores; the central part is predominantly composed of massive and breccia-like chalcopyrite–sphalerite and chalcopyrite–pyrite varieties; and the upper part and flanks are base-metal massive sulfide and barite–base-metal ores. In general, mineralogy of the ores is rather simple and is represented by sphalerite, chalcopyrite, pyrite, and galena. Fahlores, magnetite, hematite, pyrrhotite, bornite, arsenopyrite, argentite, and native gold are minor and rare.

The Gorevsky lead deposit in Krasnoyarsk Krai is hosted in Proterozoic carbonate rocks intruded by dolerite dykes (Fig. 2f). The deposit comprises three large orebodies Major, Western, and Northwestern. The lenticular, sheetlike and saddle orebodies are composed of lead and lead–zinc ores. Galena, sphalerite, and pyrrhotite are the major ore minerals. Pyrite, marcasite, boulangerite, and siderite are less abundant. Stringer–disseminated ores with zones and lenses of massive ores are predominant.

Geochemical features of base-metal massive ores were studied by many researchers (Inin et al., 1966; Kovalev et al., 2004; Gaskov et al., 2005). The base-metal massive sulfide ores were established as characterized by wide variations in trace elements including

chalcophyle As, Sb, Bi, Cd, Ga, In, Ge, Au, Ag, Se, and Te and siderophyle Co and Ni. Trace elements in various ore types and mineral are irregularly distributed; their contents range from mean global values to values with a concentration coefficient of 1000 or higher.

The contents of trace elements (In, Ag, Cd, In, Sn, Sb, Te) were measured with SR-XRF predominantly in massive and dense disseminated ores and major ore minerals (Table 1, Fig. 3). The highest In, Ag, Cd, and Sb contents were established in barite–base-metal (Ba–Pb–Zn) ore of the Zarechenskoe deposit; elevated Ni and In contents were measured in copper–zinc massive sulfide (Cu–Zn–Fe) ore of the Kyzyl-Tashtyg deposit; lower contents of all these elements were measured in base-metal massive sulfide (Pb–Zn–Fe) ore of the Korbalikha, Zakharovskoe and Yubileiny deposits. The In content in the ores of various deposits is extremely irregularly distributed and ranges from the mean global value to 69 ppm. Among base-metal massive sulfide ores, the highest average In content was established at the Kyzyl-Tashtyg (10 ppm) and Yubileiny (9 ppm) deposits, while the highest In content (69 ppm) was measured in massive pyrite–chalcopyrite ore of the Yubileiny deposit.

The In versus major ore constituents, (Zn, Cu) binaries, for ores of various deposits demonstrate different correlations between these elements. A positive correlation is observed for ores of base-metal massive sulfide deposits (Yubileiny, Korbalikha, Maleevskoe, Kyzyl-Tashtyg) (Fig. 4). Indium negatively correlates with zinc and copper at the Zarechenskoe barite–base-metal and Gorevsky base-metal deposits. A negative correlation between In and Pb was found throughout deposits.

According to measurements of the major ore minerals (sphalerite, chalcopyrite, pyrite, and galena), sphalerite and chalcopyrite are the main carriers of In (Fig. 3). In the ores of the Kyzyl-Tashtyg and Maleevskoe deposits, the highest In content was determined in sphalerite (up to 36.0 and 17.1 ppm, respectively); at the Yubileiny deposit, chalcopyrite is the richest in In (up to 51.1 ppm). In the ores of the Korbalikha deposit, an elevated indium content was measured in both sphalerite (up to 38.6 ppm) and chalcopyrite (up to 25.1 ppm), but it is distributed extremely irregularly. In the ores of the Zarechenskoe barite–base-metal deposit, in which the highest average In content (13.45 ppm) was established, the In concentration in the major ore minerals is lower than that in the ores as a whole (up to 5.02 and 5.38 ppm in sphalerite and pyrite, respectively and galena is In-free). This may indicate individual In phases in the ores or incorporation of In into other rarer minerals (fahlores, sulfosalts). Indium was not detected in galena throughout the discussed deposits; i.e., its content is below the detection limit (0.1 ppm).

In addition, elevated Cd, Ag, and Te contents were determined in the ores of these deposits. The average Cd

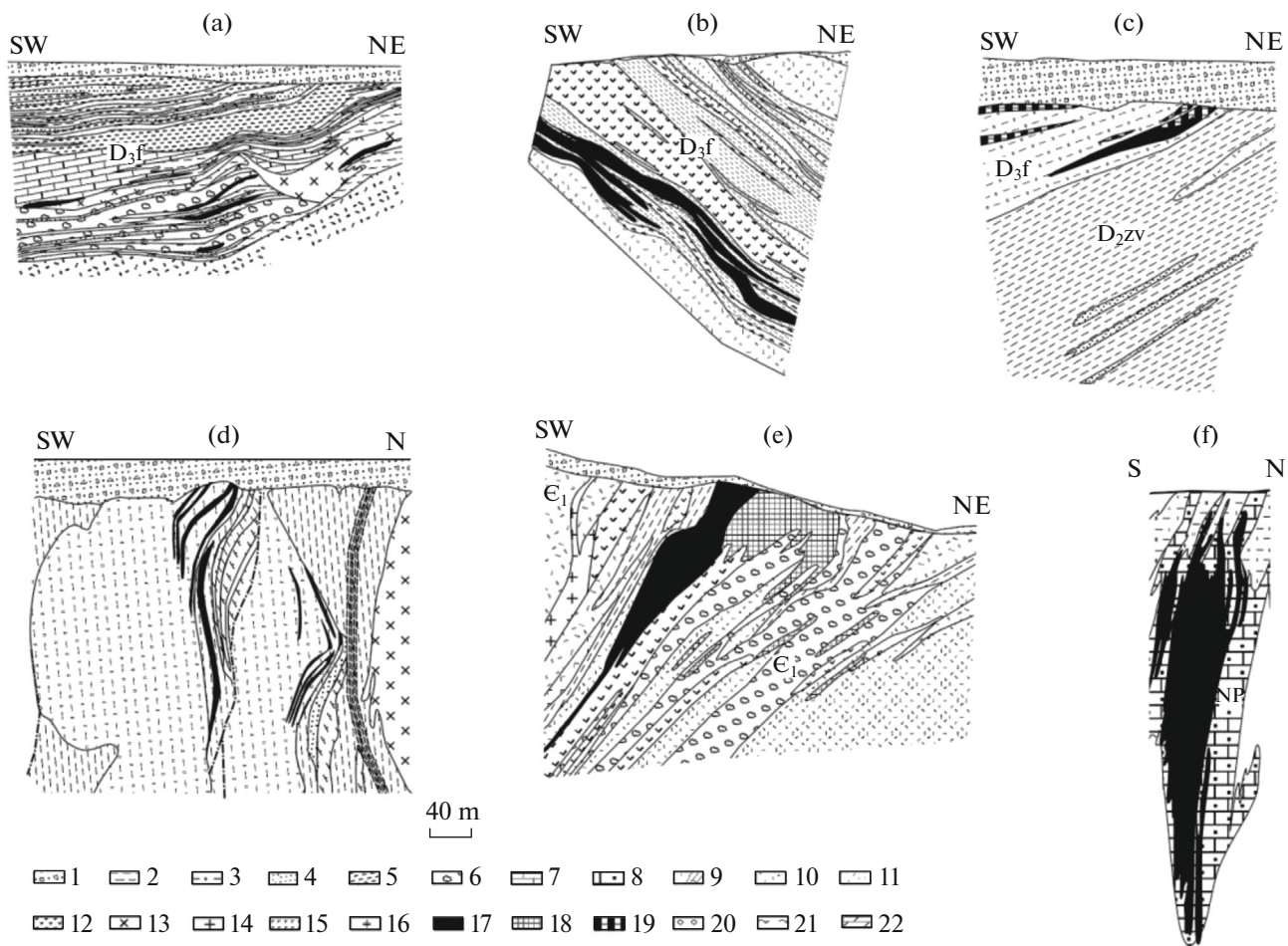


Fig. 2. Geological sections of volcanogenic base metal deposits. (A–D) Ore Altai: (A) Yubileiny, (B) Korbalikha, (C) Zakharovskoe, (D) Zarechenskoe; (E) Kyzyl-Tashtyg, Tuva; (F) Gorevsky, Yenisei Ridge. (1) Quaternary, (2) lime–clay siltstone and silty pelite, (3) quartz–sericite, mica chert and quartzite, (4) polymictic sandstone, (5) tuffstone and tuffite, (6) mixed breccia, (7) limestone and calcareous slate, (8) dolomite, ankerite, and siderite rocks, (9) calcareous breccia, (10) rhyolite and rhyodacite tuffs and flows, (11) andesidacite and andesite tuffs and flows, (12) basaltic andesite and basalt tugs and flows, (13) subvolcanic rhyolite and rhyodacite porphyries, (14) subvolcanic dacite porphyry, (15) subvolcanic porphyritic dolerite and gabbro–dolerite, (16) porphyry syenite dikes, (17) base-metal massive sulfide ore, (18) massive sulfide ore, (19) oxidized massive sulfide and massive base metal sulfide ores, (20) metamorphic porphyroblastic garnet–biotite–quartz, biotite–quartz, and quartz–plagioclase–amphibole rocks, (21) albite–potassium feldspar metasomatic rock, (22) metasomatic siderite.

content in the ores of all deposits studied here ranges from 1620 ppm (Zarechenskoe deposit) to 338 ppm (Yubileiny deposit); the Ag content ranges from 406 ppm (Zarechenskoe) to 61 ppm (Zakharvskoe), and the Te content varies from 111.5 ppm (Gorevsky) to 2.3 ppm (Yubileiny).

TIN–SULFIDE DEPOSITS

At Russian Far East tin–sulfide deposits, a high In content was established in the last century and indium reserves were estimated at some of them (Festivalny, Solnechny, Pravourmiisky, and Tigrinoe) (Gavrilenko and Pogrebs, 1992; Butova et al., 1998; Korostelev et al., 1998; Rodionov, 2005). However, indium proper was not mined at these deposits; it was produced as a by-product with melting of tin concentrate

at the Novosibirsk tin plant. Therefore, estimation of the In content in the tailing of this plant became one of the problems of this study.

Tin–sulfide mineralization in the Russian Far East is displayed within five ore clusters: Khingan, Badzhal, Komsomolsk, Arminsk, and Kavaleroovo. Most deposits are related to Cretaceous and Paleogene tin-bearing volcanic–plutonic complexes localized at an Andean-type transform or active continental margin (Khanchuk, 2000).

The Tigrinoe and Pravourmiisky deposits are the most promising for In. A review of all published data and determination of the In content in small technological samples (60–80 kg) collected from typical ores different in mineralogy at the Tigrinoe deposit and hand specimen samples of the Pravourmiisky ores

Table 1. XRF data (ppm) for ore elements in ores of massive base metal sulfide and base-metal deposits

Number of sample	Fe, %	Mn, %	Ni	Ag	Cd	In	Sn	Sb	Te
Yubileiny deposit									
Yu-1086-535	7.7	0.19	818	11.4	557	1.92	0.31	7.25	n.d.
Yu-1086-605	3.1	0.08	440	26.4	380	3.2	15	0.5	3.74
Yu-1091-493	8.41	0.22	381	30.1	460	1.33	6.68	21	0.2
Yu-1091-495	7.93	0.13	118	188	241	1.47	n.d.	590	n.d.
Yu-1091-500	15.5	0.21	57	56	65	0.45	3.76	391	n.d.
Yu1120-559	2.57	0.18	142	88	390	2.37	2.36	178	0.34
Yu1120-569	17	0.20	8.4	71	9.71	3.18	1.15	144	0.53
Yu-1120-564	22.1	0.08	679	141	634	69	1.9	218	n.d.
Yu-1120-570	2.18	0.20	202	59	392	n.d.	8.61	122	n.d.
Yu-1150-558	8.65	0.13	365	98	569	7.01	26.2	144	8.24
Yu-1150-567	3.01	0.06	29.6	2.67	21.4	0.12	1.69	3.3	0.73
Average	8.92	0.15	294.55	70.14	338.10	8.191	6.77	165	2.30
Zakharovskoe deposit									
Z-319-138	25.8	0.06	1093	62	881	n.d.	n.d.	28.9	n.d.
Z-382-158	7.18	0.024	382	15.3	330	n.d.	10.6	19.5	5.35
Z-382-159	11.5	0.04	578	26.7	489	n.d.	n.d.	89	n.d.
Z-382-169	5.22	0.03	344	12.2	262	0.85	9.41	9.07	5.49
Z-398-191	7.3	0.08	2463	60	1571	1.81	7.83	18.5	10.1
Z-542-153	26.6	0.06	342	85	607	0.54	28.4	78	18.5
Z-549-140	6.62	0.03	783	37.7	1296	1.3	16.1	37.7	10.6
Z-553-187	10.2	0.08	1812	89	1285	2.52	69	19.3	29.4
Z-575-122	9.07	0.10	273	15.9	562	0.19	14.3	4.47	7.68
Z-580a-113	16.5	0.06	1585	214	236	0.92	119	98	96
Average	12.60	0.06	965.5	61.78	751.9	0.81	34.33	40.2	22.89
Korbalikha deposit									
K-437-602	15.1	0.17	128	221	252	4.28	8.99	853	n.d.
K-437-635	6.84	0.11	2217	1698	765	14.2	71	4234	6.05
K-437-647	29.1	0.09	966	352	783	35.5	139	839	n.d.
K-414a-647	7.38	0.24	1423	312	1188	n.d.	12	563	n.d.
K-414a-662	21.8	0.11	518	166	343	1.15	96	281	5.79
K-452-1024	4.9	0.17	17.8	551	847	2.51	6.49	388	n.d.
K-453-397.6	23.7	0.10	1003	101	827	1.36	35.4	198	6.68
K-453-407	18.1	0.09	1388	139	1042	2.16	42.3	63	6.78
K-496a-641	20.6	0.12	630	224	647	3.36	49.2	257	2.69
K-496a-642	11.3	0.11	1006	153	809	2.34	21.7	136	0.87
K-471-1009	29.3	0.06	269	26.2	285	4.55	39.2	35.7	n.d.
K-552-227.5	25.8	0.06	512	13.9	498	0.42	n.d.	22.1	n.d.
Average	5.83	0.12	839.82	329.76	690.50	5.9953	47.39	655	4.8
Zarechenskoe deposit									
OZU-24	0.155	0.034	189	961	832	19.7	n.d.	10532	n.d.
OZU-27	8.21	0.185	36.8	162	105	2.45	17.2	2536	0.26
OZ-406	0.245	0.044	309	534	1015	12.7	1.68	7680	n.d.
OZ-46	6.1	0.086	1686	92	2648	n.d.	26.6	345	1.33
OZD-19	4.05	0.094	1852	75	2443	4.97	29.5	1302	0.69
OZD-28	0.82	0.045	723	440	1738	26.5	n.d.	11796	n.d.
Udachn. 1	0.14	0.201	673	608	1685	13.9	6.77	7919	n.d.
OM 35	0.52	0.201	501	378	2495	13.9	70	5985	6.42
Average	0.11	2.53	746.22	406.25	1620.12	11.775	25.29	6011.87	2.81
Maleevskoe deposit									
M-3/1	13	0.27	10.3	4.19	10	0.26	2	22.7	1.24
M-3/2	20.7	0.23	—	5.33	5.19	0.75	2.95	11.6	2.78
M-3/3	20.6	0.20	—	7.73	5.13	0.99	3.02	6.19	2.67
M-3/4	20.8	0.16	45	19.1	8.21	5.07	5.3	5.08	1.89
M-3	19.2	0.21	—	9.94	6.09	0.98	2.84	8.57	2.81
M-4	34.8	0.08	540	122	789	7.06	6.81	463	4.4
M-5	42.1	0.09	410	108	70	2.29	9.16	11.9	5.6

Table 1. (Contd.)

Number of sample	Fe, %	Mn, %	Ni	Ag	Cd	In	Sn	Sb	Te
M-6	44.1	0.08	107	46.6	34.9	10.8	3.06	61	3.51
M-7	30.3	0.36	406	146	143	8.63	1.97	14.4	0.19
M-8	24.9	0.20	1796	181	2097	18.1	8.54	49.5	n.d.
M-9	7.62	0.39	893	24.8	1008	8.34	0.86	20.4	n.d.
M-11	3.21	0.26	424	93	610	0.19	n.d.	194	n.d.
M-16	19.8	0.21	18.2	262	146	6.55	7.33	1062	1.91
Average	20.16	0.21	464.95	79.21	379.42	5.39	4.49	148	2.70
Kyzyl-Tashtyg deposit									
KT-1/1a	11.8	0.15	1613	282	980	4.71	46.8	184	56
KT-1/1b	2.09	0.15	207	51.4	267	0.65	4.33	98	3.98
KT-2/3	35.8	0.07	506	58	256	15.9	6.32	204	23.7
KT-2/4	14.4	0.18	2258	29.7	1658	19.5	5.67	37.7	7.86
KT-1/2	21.5	0.28	606	26.6	146	n.d.	6.01	11.4	6.27
KT-41	7.77	0.12	1216	178	952	n.d.	35.5	66	20.8
Average	15.56	0.16	1067	104.3	709.83	6.79	17.44	101	19.77
Gorevsky deposit									
Gor.20/9	24.5	0.39	2642	403	718	2.51	445	1758	126
Gor.7/97	20.7	1.42	2199	335	481	1.79	267	1315	75
Gor.1/97	16.9	1.73	1893	405	852	9.12	502	576	148
Gor.19/9	21.5	1.61	1319	295	608	6.32	353	779	97
Average	2.09	1.29	2013.2	359.5	664.7	4.94	391.75	1107	111.5

n.d., not detected. In the sample number column, Yu, Z, K, M, KT, and Gor denote Yubileiny, Zarechenskoe, Korbalikha, Maleev, Kyzyl-Tashtyg and Gorevsky deposits, respectively. For the Yubileiny, Zakharovskoe and Korbalikha deposits, the first and the second numbers in the sample number denote the borehole number and sampling depth, respectively. (OZU) Ore Altai, Zarechenskoe deposit, Udachnoe orebody; (OZ) Ore Altai, Zarechenskoe deposit; (OZD) Ore Altai, Zarechenskoe deposit, dumps, (Udachn. 1) Udachnoe orebody; (OM) Ore Altai, Maleev deposit.

using the SR-XRF method were applied to estimate the In content at these deposits. The In concentration in various minerals was measured with a TESCAN MIRA 3LM scanning electron microscope operating at acceleration voltage 20 kV, current intensity 1 nA, and counting time 60 s at the Analytical Center of the Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences. In addition, the tailings of the Novosibirsk tin plant, where processed ores from these and other deposits were sampled.

The Tigrinoe deposit, Primorsky krai is located in the western part of the Arminsk ore district close to the Central Sikhote-Alin Fault (Khanchuk, 2000; Gonevchuk et al., 2005). Here, there is a monoclinical siltstone sequence with subordinate intercalations of shale, sandstone, and gravel conglomerate. These flyschoid sediments are intruded by Late Cretaceous granodiorite–adamellite–granite, rare metal fluorine-bearing leucogranite, and zinnwaldite porphyry granite (Fig. 5). According to Rb–Sr and Ar–Ar dating, the deposit, which belongs to the greisen type, formed 90–70 Ma (Gonevchuk et al., 1987, 2010; Rub et al., 1991). The molybdenum mineralization hosted in apical part of the granite intrusion is the earliest there. The tin mineralization is related to topaz, zinnwaldite, and mica–fluorite greisen. The ore mineralization is represented by mineralogically and structurally various veins and veinlets (stannite–cassiterite–quartz,

cassiterite–quartz with wolframite and stannite, and other) hosted in greisen and greisenized biotite rocks and porphyry granite (Popova et al., 2013). Cassiterite (SnO_2), wolframite ($(\text{Fe,Mn})\text{WO}_4$), and stannite ($\text{Cu}_2\text{FeSnS}_4$) are the major ore minerals; kesterite ($\text{Cu}_2\text{ZnSnS}_4$), sphalerite (ZnS), galena (PbS), arsenopyrite (FeAsS), and löllingite (FeAs_2) are minor.

The major, Sn and W, and minor, Zn, Cu, Bi, Pb, In, and Cd, elements, as well as Sc, Ta, Nb, and Mo determine the economic importance of this deposit (Popova et al., 2013; Butova et al., 1998). Our study of various types of ores revealed a wide variation in indium content from 3.0 to 433.0 ppm with an average value of 65 ppm (Table 2). This highest content was measured in a sample with predominant sphalerite. In addition to In, elevated Ge (6–37 ppm), Ga (13–37 ppm), and Nb (20–66 ppm) contents were found in the ores. The In content in sphalerite of the Tigrinoe deposit, determined with an electron microprobe (30 point analyses), ranges from 1800 to 7500 ppm with an average value of 4200 ppm. The coefficient of correlation between In and Zn is 0.7. The lower In content was determined in stannite up to 240 ppm, chalcopyrite up to 900 ppm, and cassiterite up to 18 ppm (Popova et al., 2013). The total reserves of indium in the Tigrinoe ores are about 570 t (Popova et al., 2013).

The Pravourmiisky deposit, Khabarovsk krai is located in the Badzhal ore district (Khanchuk et al., 2000; Gonevchuk et al., 2005), whose area corre-

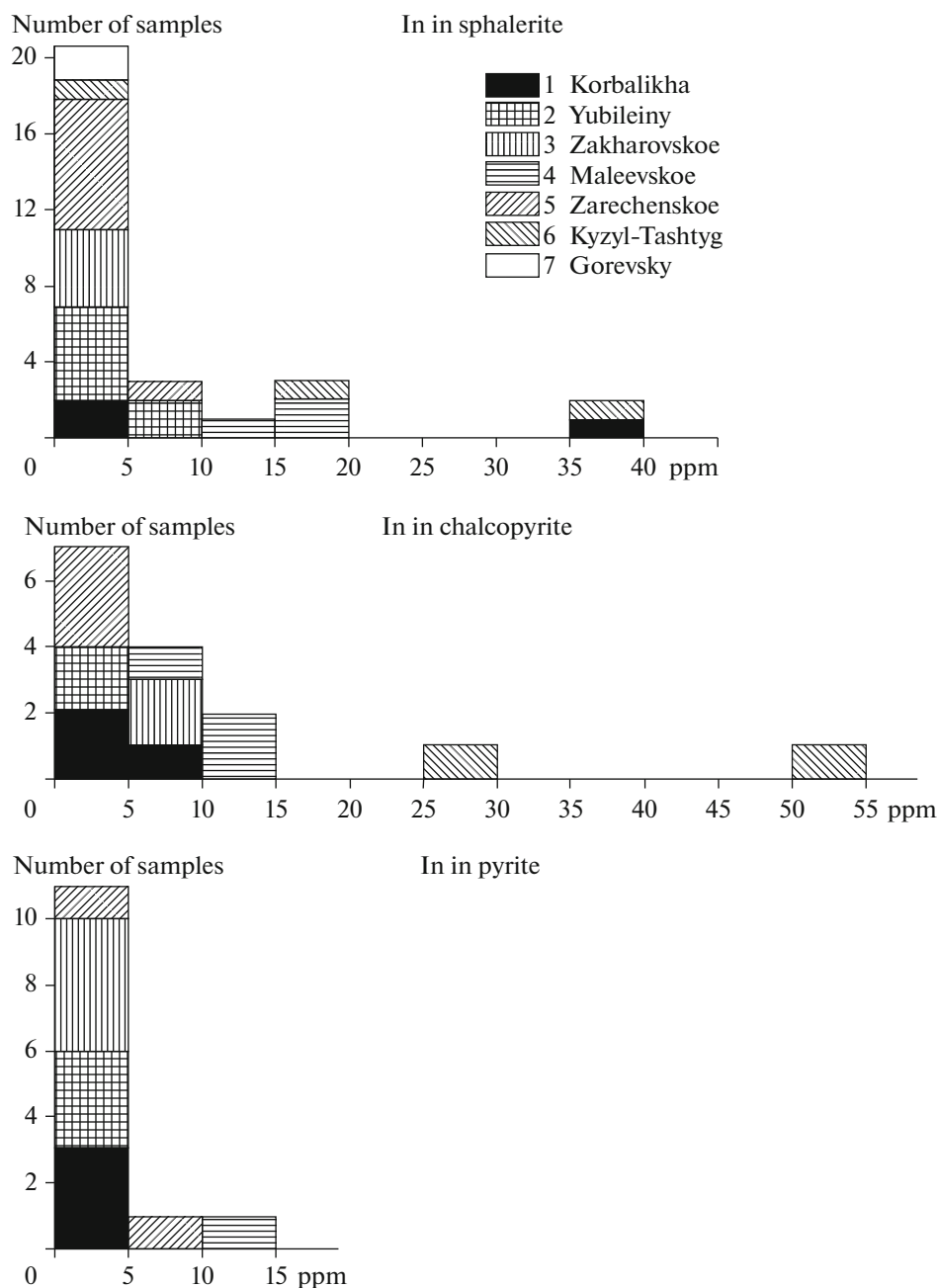


Fig. 3. Histograms for In content in various ore minerals of base-metal deposits of Siberia.

sponds to the boundaries of the eponymous volcanic zone with rocks of the Jurassic Badzhal accretionary prism as the basement. Volcanic rocks of this zone have Cretaceous intrusions (125–90 Ma) of various complexes: Dayansky alkali-basic, Laki andesitic, Badzhal granite–rhyolite, and Silinka monzonite (Maksimov, 1978; Geology of tin ..., 1986; Lebedev et al., 1999; Gonevchuk, 2002; Gonevchuk et al., 2010). This deposit is related to the eastern contact of the Upper Urmi granite pluton of the Badzhal Complex. Here, abundant porphyry granite dikes intruded

rhyolitic ignimbrite in the hanging wall of a low-amplitude thrust fault (Fig. 6) (Gavrilenko et al., 1992; Gonevchuk et al., 2010; Semenyak, 1988). The ore zone up to 17.2 m in thickness and more than 2400 m in length is composed of ore-bearing altered rocks related to the greisen process, which starts with sericite alteration of rhyolite and granite. Cassiterite and wolframite as the most important ore constituents and some sulfide minerals belong to the siderophyllite–quartz–topaz and quartz–topaz assemblages that formed at the late stage of the greisen process (Panova

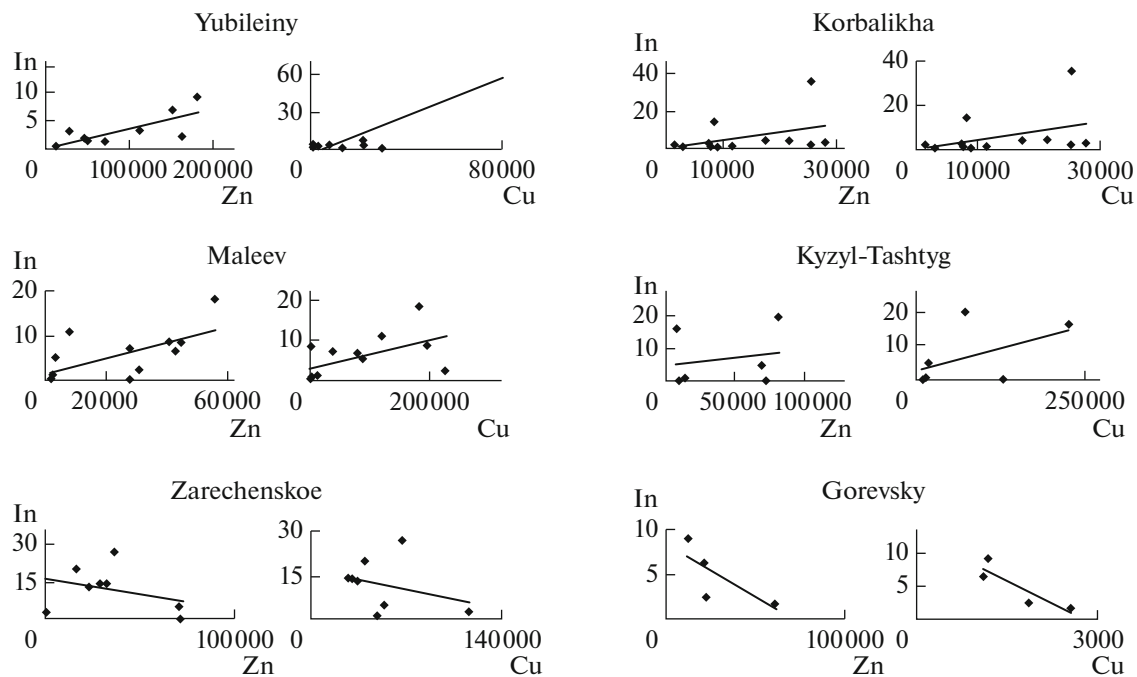


Fig. 4. Correlation plots between In and major ore elements in base-metal deposits of Siberia.

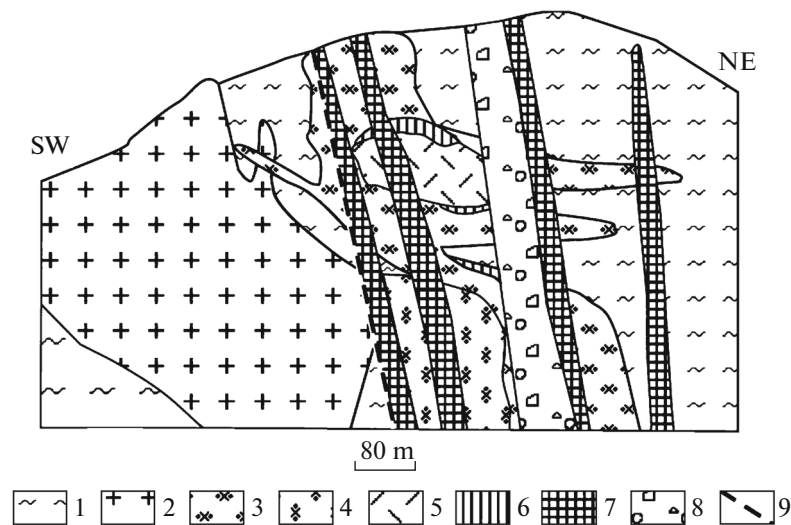


Fig. 5. Geological section of Tigrinoe deposit, after Gonevchuk et al. (2005). (1) Biotite rock replacing sedimentary rock, (2) porphyry granite of Glavny (Main) stock (phase I), (3) greisenized porphyry granite of Maly (Small) stock (phase II), (4) greisenized porphyry granite with pot-shaped quartz, (5) massive tin-bearing greisen (Tigrenok body), (6) stockscheider, (7) ore stockwork, (8) projection of explosion hydrothermal breccias, (9) fault.

et al., 1993). Predominantly tourmaline veins with disseminated sulfides formed at the final stage. Scattered quartz–feldspar veinlets with molybdenite and rare fine-grained scheelite, wolframite, löllingite, cassiterite, and bismuth minerals were opened at the deep level of the deposit by boreholes (Semenyak et al., 1997). High contents of cassiterite, wolframite, arsenopyrite, chalcopyrite, and bornite, as well as less fre-

quent sphalerite, pyrite, pyrrhotite, stannoidite, monsonite, and stannite, determine the economic importance of the deposit.

Gavrilenko and Pogrebs (1992), who studied in detail the In content in the ores and minerals of the Pravourmiisky deposit, showed that tin deposits are one of the important sources for economic indium. According to their data, the highest In concentration

Table 2. XRF, atomic absorption (*), and ICP-MS (**) data (ppm) for indium and other elements in ores of Tigrinoe and Pravourmiisky deposits, Russian Far East

Sample	Cu	Zn	As%	Ag	Ga	Ge	Nb	Y	Zr	In	In*	In**
Tigrinoe deposit												
1	1337	2783	0.50	19.5	19.8	9.5	21.3	133	71	3.0	<5	
2	343	14377	2.5	22.4	21.4	52.9	37.7	33.6	8.7	40.5	28	
3	1941	25259	8.3	24.4	15.6	29.7	40.3	26.2	8.4	56	37	
4	474	1265	1.12	4.0	15.4	11.0	33.8	17.8	23.3	3.0	<5	
5	738	1946	0.05	2.2	15.9	5.6	66	14.8	15.6	8.1	<5	
6	7253	20607	7.0	22.2	16.8	12.4	30.8	29.6	14.9	6.5	8.5	
7	756	4281	0.2	5.6	12.6	23.9	33.6	17.1	12.9	6.1	<5	
8	1482	105735	19.9	13.9	37	37.0	20.1	28.2	16.1	400	433	
Pravourmiisky deposit												
1-86	15684	259	15.6	11.8	7.6	43.8	7.5	9.0	35.5	36.8	22	39
118-87	1201	165	28.8	27.4	19.0	85.0	18.8	6.0	13.9	120	109	
138-87	1023	77	3.1	3.3	5.4	47.6	2.5	27.5	43.4	8.3	<5	1.2
153-83	108993	859	21.4	129.0	11.7	19.7	8.8	6.0	46.5	30.3	29	
18-87	41768	711	5.5	15.0	11.8	58.0	9.9	12.6	72	35.2	37	32
26-87	13120	332	5.3	7.6	1.5	6.6	3.9	27.1	112	38.2	36	
40-86	40285	390	11.2	45.3	9.5	31.1	10.9	5.0	5.0	130	115	
57-86	3775	284	4.1	2.8	6.7	10.2	3.8	10.7	98	9.1	15	
7-86	15477	447	0.1	5.8	4.4	7.2	5.0	24.7	130	47	26	
72-86	302935	598	2.4	35.2	3.6	16.8	4.9	16.8	64	111	110	
Tailing of Novosibirsk tin plant												
Sn-z 1	3884	3888	7.5	61	—	—	—	—	—	31.5	29	
Sn-z 2	3403	3777	7.7	38.8	—	—	—	—	—	19.3	16	
Sn-z 3	3868	3171	6.1	84	—	—	—	—	—	20.7	23	
Sn-z 4	13301	4416	2.6	197	—	—	—	—	—	38.3	32	
Sn-z 5	9527	3383	3.4	111	—	—	—	—	—	24.5	16	18
Sn-z 5	9789	3556	3.8	154	—	—	—	—	—	32.8		
Sn-z 5	5738	2168	2.3	78.0	12.6	14.0	5.3	79	180	20.5		
Sn-z 6	6428	6125	8.9	61	—	—	—	—	—	40.0	54	44

(up to 3600 ppm) was found in sphalerite; in chalcopyrite and bornite it is 1300 and 170 ppm, respectively. Cassiterite and wolframite as the major constituents of the deposit have the low In content 7.2 and 5 ppm, respectively.

According to our data (Table 2), the In content in the ore hand specimens of the Pravourmiisky deposit ranges from 5 to 130 ppm (average of 20 analyses is 55 ppm). The highest In content (111–130 ppm) is characteristic of chalcopyrite- or bornite-dominant samples (total 25–35 vol %). Sulfide minerals (sphalerite, chalcopyrite, stannite) typically have the highest In content; cassiterite has a lower concentration. According to electron microprobe data, the In concentration in sphalerite and stannite ranges from 100 ppm to 2.4 wt % and from 2 to 6 wt %, respectively; in chalcopyrite it reaches 1.4 wt %. Indium is most frequently incorporated into sulfide minerals as an isomor-

phic admixture and only occasionally does it form individual mineral roquestite (CuInS_2) as fine intergrowths with sphalerite in chalcopyrite (Korostelev et al., 1998; Gavrilenko et al., 1992). It is interesting that sulfide mineralization at the Pravourmiisky deposit is related to siderophyllite–quartz–topaz alteration, which is also characterized by a high In content (40–113 ppm) at the Mangabeira deposit (Moura et al., 2007). This indirectly indicates additional resources of this element at the deposit. Total reserves for indium in Pravourmiisky ores are 402 t (Onikhimovsky et al., 1996).

A high indium content was also determined at other tin deposits. For example, the In concentration in sphalerite from the Ege-Khaya and Deputatsky deposit is 90–4700 and 50–3400 ppm, respectively (Indolev and Nevoisa, 1974). In the ores of the Vysokogorny deposit, in which indium mineral proper was found, the In content ranges from 20 to 300 ppm

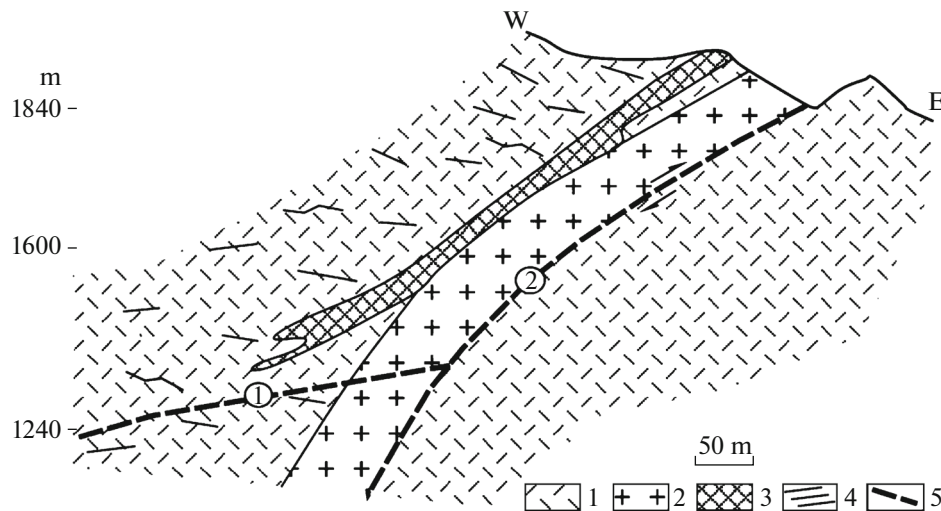


Fig. 6. Geological sketch section of Pravouriisky deposit, after Rodionov (2005). (1) Rhyolite ignimbrite, (2) porphyry granite dike, (3) ore zone with quartz-topaz greisen with tin-sulfide mineralization, (4) stinger-disseminated mineralization in gentle fractures, (5) faults: (1) South zone, (2) contact fault.

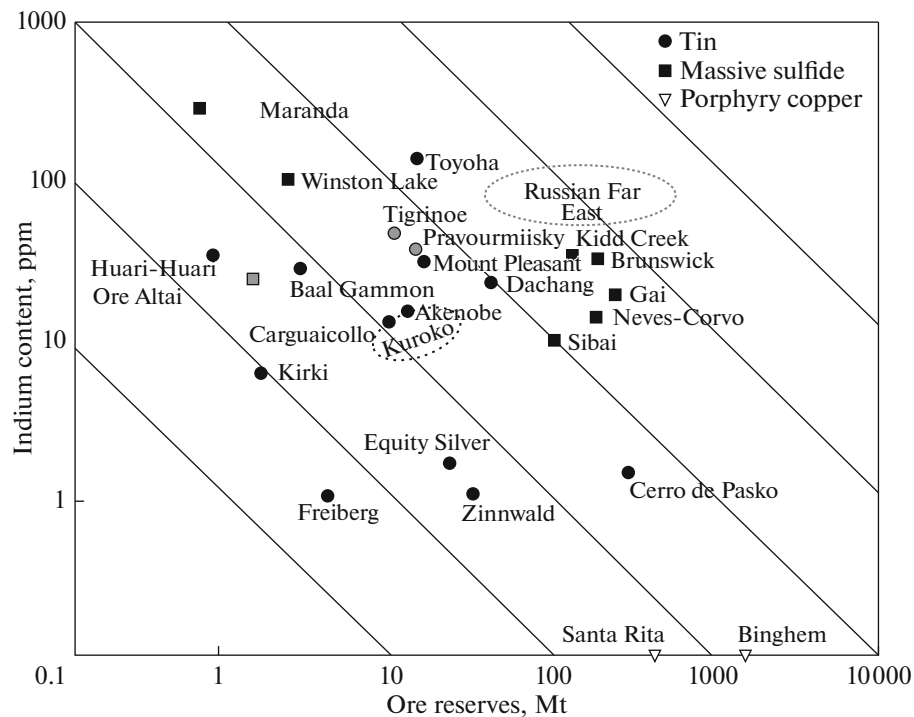


Fig. 7. Tin content and reserves in ores of various deposits.

(Kokin et al., 2010). The indium reserves were preliminarily estimated at the Festivalny (279 t) and Soboliny (33 t) casiterite-sulfide deposits in the Komsomolsk ore district and at the Arsenevsk deposit (900 t) in the Kavalerovo tin district (Gonevchuk et al., 2006; Onikhimovsky et al., 1996).

The study of samples from the Novosibirsk tin plant revealed an elevated In content (the average from

16 analyses is about 30 ppm), which is comparable with the In content in ores of massive sulfide and tin deposits and it can be regarded as an alternative source of indium (Table 2). In addition, the XRF study revealed a significant silver content in tailings of up to 154 ppm, as well as Ge, Cu, Zn, and other elements.

Elevated indium and other rare element (Cu, Zn, Pb, As, Sb, Sn, W, Bi) contents were also established

in the tailings of the Solnechny and Central ore-processing plants, where ores from the Solnechny, Perevalny, Peridorozhny, and Festivalny deposits of the Komsomolsk ore district were processed. The tailings, with a total volume of 35 Mt, contain about 170 t of indium (Khanchuk et al., 2012).

CONCLUSIONS

(1) The study of the indium content in base-metal massive sulfide and tin–sulfide deposits of Siberia and the Russian Far East and a review of literature concerning this problem showed that the In content at these deposits exceeds the overall average at similar deposits worldwide; therefore, these deposits are of economic interest.

(2) The indium content and its distribution at the Tigrinoe and Pravourmiisky tin deposits, and preliminarily estimated indium reserves for them as 570 and 402 t, respectively, showed that these deposits correspond to economic indium deposits and are comparable with indium deposits worldwide (Fig. 7).

(3) Sulfide minerals are the major In carriers in the ores: sphalerite and chalcopyrite at base-metal massive sulfide deposits, and chalcopyrite, bornite, and sphalerite at greisen tin–sulfide deposits.

(4) High Cd (up to 1620 ppm), Ag (406 ppm), and Te (up to 111.5 ppm) contents were established in the ores of base-metal massive sulfide deposits, whereas elevated Ge (up to 37 ppm), Ga (up to 37 ppm) and Nb (up to 66 ppm) contents were measured in the ores of tin–sulfide deposits. This has stimulated the investment attractiveness of these deposits.

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