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Sikhote Alin as a Possible Province of Hydrothermal Sedimentary Gold, Silver, PGE, Tin, Zinc, Lead, and Tungsten Deposits

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The Triassic–Jurassic carbonaceous sequence of Sikhote Alin contains metalliferous sediments composed of siliceous–rhodochrosite rocks and their metamorphosed analogues (mainly, manganese silicates and aluminosilicates) [2], pyrophanite-bearing siliceous rocks (hereafter, brown cherts), tin–iron ores, ilmenite– biotite–feldspar rocks, and itabirites. Metalliferous sediments of all types have high contents of Au, Ag, and PGE.

Manganese rocks are mainly composed of rhodonite, pyroxmangite, and Mn-garnet. In some places, they contain kanoite, tephroite, pyrosmalite, tirodite, manganactinolite, pyrophanite, rhodochrosite, helvite, sphalerite, galena, chalcopyrite, wolframite, scheelite, K-feldspar, albite, Mn-chlorite, native silver, highgrade gold [3], porpezite, and other minerals. The manganese rocks are characterized by the presence of graphite, barite, Ba-feldspar, Ba-phlogopite, monazite, apatite, and various compounds of Ni and Co [1, 2].

The chocolate-brown cherts (metamorphosed radiolarites with a clayey admixture) consist of quartz, Baand As-bearing mica-type minerals, and pyrophanite. They contain orthite, monazite, cassiterite, zircon, cobaltite, argentite, and native iron. Spessartine, graphite, rutile, barite, galena, $(Cu,Zn)Fe₂S₃$, chalcopyrite, native gold, halite, and sylvite are subordinate minerals. The cherts are characterized by the abundance of microscopic dissemination of gold and argentite, as well as submicroscopic dispersion of minerals of Ag, Pd, Rh, Ru, Au, Os, Ir, and Pt [2].

Tin–iron ores are represented by talc–chlorite–magnetite and manganactinolite–magnetite varieties. The talc–chlorite–magnetite ores include ilmenite, sphene, cassiterite, spessartine, sphalerite, quartz, xenotime, Sn-bearing silicate, and apatite [2]. The amphibole– magnetite ores contain spessartine, sphalerite, cassiterite, native lead, and La–Ce–Nd oxide [2]. They also include apatite, $Fe_8(PO4)_3SO_4(OH)_5$, NiFe S_2 , silver grains with up to 0.92 wt % Rh, and high-grade gold (up to 10–15 µm in diameter). Submicroscopic and dispersed particles of minerals of Ag, Au, Pt, Os, Ir, Pd, Rh, Ru, and Sn are abundant in the tin–iron ores.

The ilmenite–biotite–feldspar rocks (contact-metamorphosed metalliferous sediments) are heavy dark gray microgranular aggregates that are apparently indiscernible from the carbonaceous mudstones and silty mudstones. They are primarily composed of K-feldspar, biotite, cordierite, ilmenite, and sphene. Secondary minerals are represented by willyamite $(Co_{0.12-0.50}Ni_{0.88-0.50})_{1.00}SbS$, galena, pyrrhotite, sphalerite, chalcopyrite, apatite, barite, $Ca(Mn,Fe)_{2}Ti_{3}O_{9}$, and native Ni with gold up to 11.01 wt %. Microscopic gold and silver grains are also present. In addition, the rocks contain numerous inclusions of a Co–W ($Co_{0.00-0.60}W_{1.00-0.40}$) solid solution up to 1–5 mm in diameter. The Co–W solid solution makes up inclusions (up to $15 \mu m$ across) in some pyrrhotite grains (Fig. 1).

Itabirites are cherry red or brown radiolarites with rutile, hematite, and subordinate hydromica. They are irregularly reduced (hematite and hydromica are replaced by chlorite) and crosscut by chlorite stringers. The itabirites contain monazite, apatite (with monazite inclusions), zircon, Sn-bearing native copper, native iron, and Ba-bearing feldspar veinlets (Table 1). They always include silver (Fig. 2) and high-grade (fineness 851) gold particles up to 0.1 mm in diameter.

Hydrothermal ores are associated with syngenetic metalliferous sediments that represent brown, brownish, or reddish cherts with numerous recrystallization patches and leaching cavities. In some places, they contain stringers and nests of Mn-silicates, pyrolusite, and hydroxides of Mn and/or Fe that represent products of

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Fig. 1. Inclusion of the cobalt–tungsten solid solution in pyrrhotite. (a) BSE image; (b–d) characteristic radiation images of W, O, and S, respectively.

the alteration of brown cherts, itabirites, and ordinary cherts. Such rocks include native iron, phosphide $Ni₅P$, monazite, cassiterite, wolframite, native antimony, antimonite, Zn–Zr–Ti oxides, Zr–Sc oxides, barite, chlorargyrite, lead sulfate, and silver sulfate (Table 2). They are characterized by an abundance of aggregates of silver, argentite, and gold grains (up to 0.5 mm in diameter). Pd, Rh, Ru, Au, Os, Ir, and Pt occur as submicroscopic and microscopic dispersion.

Hydrothermal noble metal mineralization is also observed as an amphibole (with pyroxene, spessartine,

Ord. no.	Ω	Al	Si	P	Ca	Ti	Fe	Zr	Au	Cu	Ag	Total
									85.07		14.93	100.00
2	53.51	1.09	23.62			23.12	0.49					102.28
3										89.41		100.00
$\overline{4}$							98.90					99.98
5	38.67	0.73	8.55	14.88	29.82	0.43						98.96
6	42.84	0.93	12.14			18.48	19.34					96.26
7	50.03	9.74	28.38									100.00
8	36.57		15.56					47.2				99.32
9	36.90	0.28	32.17								25.51	100.63

Table 1. Compositions of minerals in itabirites of the Shirokaya Pad area

Note: (1) Gold (from panned sample) $Au_{0.76}Ag_{0.24}$; (2) rutile $(K_{0.02}Fe_{0.02}Al_{0.07}Ti_{0.89}l_{1.00}O_{1.93} \cdot 1.13H_2O$ (including 0.46 wt % K); (3) native copper Sn_{0.06}Cu_{0.94} (10.59 Sn); (4) native iron Mn_{0.01}Fe_{0.99} (1.08 Mn); (5) apatite (K_{0.05}Ti_{0.06}Sr_{0.08}Al_{0.17}Ca_{4.64})_{5.00}(PO₄)₃(OH)_{1.58} (7.36 C, 0.34 K, 1.11 Sr, 2.24 Te); (6) ilmenite ($Mg_{0.07}Mn_{0.08}Fe_{0.84}$)_{0.99}($Al_{0.08}Ti_{0.93}$)_{1.01}O_{2.97} · 1.4H₂O (0.65 Mg, 1.87 Mn); (7) K-feld- $\mathrm{span}\left(\mathrm{Ba}_{0.02}\mathrm{Na}_{0.07}\mathrm{K}_{0.78}\right)_{0.87}\mathrm{Al}_{1.08}\mathrm{Si}_{3.04}\mathrm{O}_{8.15}\cdot1.24\mathrm{H}_2\mathrm{O}$ (0.56 Na, 10.17 K, 1.12 Ba); (8) zircon Zr $_{0.92}\mathrm{Si}_{0.99}\mathrm{O}_{4.09};$ (9) silver Ag $_{1.00}$ (5.77 C). Here and in Tables 2–5: (1) the presence of C is related to the sputtering of polished samples with graphite; (2) in the case of small sizes of grains, microprobe analyses are often related to zones composed of two or more minerals, and mineral formulas are calculated from their bulk compositions.

Fig. 2. Native silver in itabirite of the Shirokaya Pad area. BSE image.

or garnet of the grossular–andradite series) or greenish and yellowish pink pyroxene-rich rocks formed after calcareous rocks. Amphibole is represented by manganactinolite (tremolite) or dannemorite, while clinopyroxene is represented by mangansalite. These rocks contain abundant sphalerite and willemite in some places. Galena, $InPO₄$, cassiterite, magnetite, native metals (tellurium, bismuth, silver, and gold), monazite, and $PbSn₃O₇$ are subordinate minerals. Native gold occurs as dispersion and aggregates of variable dimension characterized by a maximum fineness (Tables 3, 4). Hydrothermal ores are products of the regeneration of metalliferous sediments. They formed in the course of hydrothermal activity in the course of the evolution of Late Cretaceous granitoid massifs.

Metalliferous sediments are widespread over large areas of the Ol'ga, Dal'nerechensk, and Dal'negorsk ore districts. In general, they are Middle–Late Triassic formations. However, the itabirites can be Middle–Late Triassic and Jurassic rocks. The metalliferous sediments are also typical of other ore districts in Sikhote Alin. In these districts, the itabirites and brown cherts could be mistaken for ordinary cherts, while the manganese rocks could be ignored in the course of geological surveys, as in the case of the Dal'nerechensk ore district and a significant area of the Ol'ga ore district. The metalliferous sediments are developed in the Shirokaya Pad and Mokrusha areas of the Ol'ga ore district [2]. In the Shirokaya Pad area, they make up at least one 5-m-thick ore-bearing sequence that can be divided into two units. The Middle–Late Triassic brown chert unit includes a bed of manganese rocks near the upper contact. The total thickness of the overlying bed of tin–iron ores varies from tens of centimeters to a few meters. The ore-bearing sequence is developed over an area of no less than 20 km2 . This sequence is presumably underlain by itabirites and ilmenite–biotite–feldspar rocks. The Middle–Late Triassic itabirite unit (>4 m thick) contains Au, Ag, and, probably, PGE. The thick-

Fig. 3. Gold (white patches and points, including the barely discernible ones) in the amphibole–pyroxene rock of the Shirokaya Pad area (BSE image). At the left lower corner, one can see three zinc oxide grains (white) with abundant platinum dissemination.

ness and stratigraphic position of the ilmenite–biotite– feldspar unit are unclear.

The metalliferous sediments incorporate numerous hydrothermally altered cherts and amphibole–pyroxene rocks with high contents of noble metals (Fig. 3). All types of metalliferous sediments and hydrothermally altered rocks are characterized by an abundance of dispersed, submicroscopic, and microscopic dissemination of Sn, Ag, Pd, Rh, Ru, Au, Os, Ir, and Pt in ore minerals and enclosing rocks.

The Shirokaya Pad area has several attributes of a giant stratiform tin–noble metal deposit. The assay and ICP-MS analyses of manganese rocks have revealed the presence of Au (up to 35 g/t), Pt $(0.08-0.33 \text{ g/t})$, Zn (up to 5.97 wt %), Cu (up to 0.64 wt %), Ni (up to 0.14 wt %), Co (up to 0.10 wt %) [1], and Pb (up to 1.04 wt %). According to acid leaching data, nearly each sample contains Au from *n* to 100 g/t (approximate estimate with the consideration of sample weight, number of extracted grains, and their average diameter). Microprobe data indicate that the metalliferous sediments contain a significant amount of Sn, Ag, and PGE.

The Mokrusha area incorporates noble metal ores of at least two types (manganese rocks and amphibole– pyroxene rocks with occasional magnetite). The manganese rocks contain abundant palladium gold (porpezite) with Ag admixture (Fig. 4, Table 5), as well as Agand Pd-free gold. The amphibole–pyroxene rocks contain pure native gold and silver (Table 4).

In the Dal'nerechensk district, metalliferous sediments are represented by manganese rocks [3], itabirites, and, probably, brown cherts. The manganese rocks contain Ga (up to 709.8 g/t), Au (up to 8.43 g/t), Pt (up to 1.54 g/t), Pd (up to 5.33 g/t), Zn (up to 0.55 wt %), and Ni (up to 0.13 wt $\%$) [1]. These rocks make up conformable lenticular and stratiform bodies (tens of centimeters to a few meters thick) extending over tens to hun-

Table 2. Compositions of minerals in altered cherts of the Shirokaya Pad area **Table 2.** Compositions of minerals in altered cherts of the Shirokaya Pad area

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 $({\rm Fe_{0.04}Mn_{0.93}})_{0.97}$ (${\rm W_{0.02}Ti_{1.01}}$)1.03

 $O_{3,24}$ (1.72 W); (33) zircon ((Fe_{0.02}Sr_{0.03}Mn_{0.05}Zr_{0.95})_{1.05}(Ti_{0.02}Si_{0.93})_{0.95} (1.52 Sr). The presence of Cr is related to the dichromate admixture.

Ord. no.	${\rm O}$	Mg	${\rm Al}$	Si	Ca	$\rm Cr$	Mn	\mathbf{P}	${\bf S}$	$\rm Fe$
$\mathbf{1}$	13.47	0.37		4.38	2.59	8.82	0.98			6.21
$\sqrt{2}$	33.57	4.30		19.82	8.19		4.09			14.91
3	18.27	0.74		6.18	0.91		0.37			5.22
$\overline{4}$	14.66	0.66		3.95	1.15		0.39			2.46
$\sqrt{5}$	11.63			$2.00\,$	0.78					1.74
6	3.77			0.36						1.10
$\boldsymbol{7}$	33.37		1.38	1.25				11.99		1.23
$\,8\,$							0.53		33.61	6.86
9	30.55			0.88	0.31		0.44			66.62
$10\,$	31.21		0.27	27.46		0.79				11.73
11	27.96			12.19			0.24			0.9
12	29.19				0.71			14.29		
13	34.13		0.53	1.31		1.72				1.56
14	40.64	4.26		23.95	8.34		3.24			17.12
15	40.68	3.82		23.58	16.89		4.8			10.19
Ord. no.	Sn	W	\rm{In}	${\bf Zn}$	${\rm Au}$	Ag	La	\rm{Ce}	$\rm Nd$	Total
$\mathbf 1$				1.08	59.72					97.62
\overline{c}					14.16					100.00
$\overline{\mathbf{3}}$				1.62	69.79					103.11
$\overline{4}$						74.06				97.34
5						83.84				99.99
$\sqrt{6}$						92.34				97.57
τ			47.60	1.77						98.59
$\,8\,$				61.55						102.55
9										98.8
10										100.00
$11\,$				56.82						98.11
12						$2.15*$	15.24	28.40	10.00	99.98
13	61.09	1.49								101.84
14										97.54
15										99.95

Table 3. Compositions of minerals in pyroxene–amphibole rocks of the Shirokaya Pad area

Note: (1–3) Native gold (including in an. 0.96 wt % Te); (4–6) native silver; (7) indium phosphate $(Fe_{0.05}Zn_{0.06}In_{0.92})_{1.03}$ (Si_{0.10}Al_{0.11}P_{0.86})_{0.98}O_{4.00}; (8) sphalerite (Mn_{0.01}Fe_{0.12}Zn_{0.89})_{1.02}S_{0.99}; (9) magnetite; (10) native tellurium (28.54 wt % Te); (11) willemite $(Mn_{0.01}Fe_{0.04}Zn_{1.97})_{2.02}Si_{0.99}O_{4.00}$; (12) monazite; (13) cassiterite; (14) manganactinolite $(Ca_{1.95}Mn_{0.05})_{2.00}(Mn_{0.50}Mg_{1.64}Fe_{2.87})_{5.01}Si_{7.99}O_{20.99}(OH)_{2.00}$; (15) mangansalite. (*) Evidently, Th (instead of Ag) is present.

dreds of meters. The ore bodies are exposed as linear zones parallel to the strike of enclosing rocks. Some zones can be traced over 1.5 to 6.5 km on the basis of rare exposures. The stratigraphic position of itabirites is unclear. Their age may be Triassic or Jurassic. In the Dal'negorsk district, the metalliferous sediments are represented by the hydrothermally altered manganese rocks [2] and, probably, itabirites. They incorporate hydrothermal alteration zones with high concentrations of native silver, gold, and, possibly, platinum group metals.

In Sikhote Alin and some other regions of the world [4], exposures of manganese rocks make up two chains along long-lived deep faults that separate the subsided block of the earth's crust (synclinorium and megasynclinorium) from two uplifted blocks (anticlinoriums and meganticlinoriums). In some places, such faults are recognized on the basis of exposures of serpentinites or apogabbro amphibolites. The metalliferous sediments in the Triassic–Jurassic carbonaceous sequence of Sikhote Alin were presumably produced by numerous submarine hydrothermal sources confined to the Pri-

Ord. no.	Ω	Mg	Al	Si	S	Ca	Mn	Fe	Te	Au	Ag	Total
	35.23			20.18		7.4	0.77	0.62		31.36		95.57
2	11.52		1.04	4.47		1.26	2.29	1.66			77.76	100.00
3	25.11		0.35	12.65		6.92	11.23	4.80			38.93	99.99
$\overline{4}$	1.29			0.4	32.75	0.7	0.37	5.16				102.44
5	25.65			1.3		0.19	0.71	67.67				95.51
6	37.05	3.04		22.95		16.43	6.51	9.01	1.37			96.36
7	36.93	3.32		22.79		16.73	6.43	9.16				95.36
8	36.8		4.63	16.7		23.49	1.55	13.07	1.47			97.7
9	35.21		0.97	16.24		22.47	1.41	19.4	1.64			97.34
10	39.2		9.66	17.49		22.6	3.18	3.26	1.95			97.75
11	37.88	1.35	0.22	22.28		2.81	8.82	22.14				95.5
12	38.17	2.1		22.26		2.77	9.15	19.84				94.29

Table 4. Compositions of minerals in pyroxene–amphibole rocks of the Mokrusha area

Note: (1) Native gold; (2, 3) native silver; (4) sphalerite $(Mn_{0.01}Fe_{0.09}Zn_{0.91})_{1.01}S_{0.99}$ (61.78 wt % Zn); (5) magnetite ($(Mn_{0.03}Fe_{2.97})_{3}O_{4}$; (6, 7) mangansalite Ca_{1.00}(Mg_{0.30}Mn_{0.29}Fe_{0.39})_{0.98}(Te_{0.02}Si_{1.99})_{2.01}O_{6.00} and Ca_{1.01}(Mg_{0.33}Mn_{0.28}Fe_{0.40})_{1.01}Si_{1.98}O_{5.98}; (8–10) garnet (Mn_{0.13}Ca_{2.88})_{3.01}(Mn_{0.01}Al_{0.84}Fe_{1.15})_{2.00}(Te_{0.06}Si_{2.93})_{2.99}O_{11.99}, (Mn_{0.13}Ca_{2.87})_{3.00}(Al_{0.18}Fe_{1.78})_{1.96}(Te_{0.07}Si_{2.96})_{3.03}O_{12.00}, and $(Mn_{0.27}Ca_{2.68}Fe_{0.03})_{2.98}(Ti_{0.04}Al_{1.70}Fe_{0.25})_{1.99}(Te_{0.07}Si_{2.96})_{3.03}O_{12.04}$ (including 0.41 wt % Ti in analysis 10); (11, 12) dannemorite $(\overline{Ca_{0.70}Al_{0.08}Mg_{0.56}Mn_{1.70}Fe_{3.98}})_{7.02}Si_{7.98}O_{22.02}(OH)_{2}$ and $(Ca_{0.71}Mg_{0.88}Mn_{1.70}Fe_{3.63})_{6.92}Si_{8.08}O_{22.08}(OH)_{2}$.

Table 5. Compositions of minerals in manganese rocks of the Mokrusha area

Ord. no.	\mathbf{O}	Mg	Al	Si	$\bf K$	${\bf S}$	Ca	Cr	$\rm Ti$	Mn
$\mathbf{1}$	7.75		1.53	3.32			2.13			14.03
$\mathbf{2}$	18.06		3.11	4.79			1.02			13.91
$\overline{\mathbf{3}}$	18.62	0.30	1.21	2.69			1.53	1.02		10.67
$\overline{4}$	16.92			7.45			0.76			7.25
5	5.73						0.71			3.25
$6***$	15.38		0.58	1.24			2.28			8.64
τ	20.93				1.66		0.32			23.80
$\,8\,$	8.25		0.48				1.10			8.21
9	16.21		3.95	6.55			2.71			36.73
$10\,$	25.00				0.50					8.67
11						38.92				$0.4\,$
12	38.04		10.31	16.89			2.52		0.24	26.34
Ord. no.	Fe	Cu	Ba	Rb	Co	Pd	Ag	Th	Au	Total
1	1.60					1.91	2.52		65.16	99.95
$\boldsymbol{2}$						1.33	1.49		56.29	100.00
$\overline{3}$	1.98					2.80	2.83		56.34	99.99
$\overline{\mathcal{L}}$	0.77					4.43	3.81		57.97	99.36
5				1.66				$1.39*$	87.00	99.73
$6***$	1.13	0.64				2.78	5.88		60.69	100.03
$\boldsymbol{7}$	0.48		1.10						51.70	106.2
$\,8\,$	1.24					2.78	2.60		75.32	99.98
9	1.45								32.38	99.98
$10\,$									85.60	98.75
$11\,$	58.9				0.22					98.45
12	2.1									96.44

Note: (1–10) Native gold; (11) pyrrhotite; (12) garnet. Mineral formulas (native gold composition normalized to 100% is given in parentheses): (1) $Pd_{0.05}Ag_{0.06}Au_{0.89}$ (2.74 Pd, 3.62 Ag, 93.63 Au); (2) $Pd_{0.04}Ag_{0.04}Au_{0.92}$ (2.25 Pd, 2.52 Ag, 95.23 Au); (3) $Pd_{0.10}Ag_{0.08}Au_{0.82}$ (4.52 Pd, 4.57 Ag, 90.91 Au); (4) $Pd_{0.11}Ag_{0.10}Au_{0.79}$ (6.69 Pd, 5.75 Ag, 87.55 Au); (5) (87.00 Au); (6) Cu_{0.03}Pd_{0.07}Ag_{0.13}Au_{0.77} (0.91 Cu, 3.97 Pd, 8.40 Ag, 86.71 Au); (7) Au_{1.00} (100 Au); (8) Pd_{0.06}Ag_{0.06}Au_{0.88} (3.44 Pd) $(3.44 \text{ Pd}, 3.22 \text{ Ag}, 93.33 \text{ Au});$ (9) Au_{1.00} (100 Au); (10) Au_{1.00} (100 Au); (11) $(Co_{0.003}Fe_{0.87}O_{0.873}S_{1.00};$ (12) $(Fe_{0.19}Ca_{0.32}Mn_{2.45})_2.96(Ti_{0.03}Al_{1.95})_0.98Si_{3.06}O_{12.13}$. (*) Actually, a small amount Ag and Pd (instead of Th) is present;
(**) including 0.79 wt % Na.

Fig. 4. Particles of Pd-bearing gold (white rounded segregations and points mainly confined to black stringers filled with manganese and iron ochers) in manganese rocks of the Mokrusha area). Large crystals and black patches are quartz grains; rounded fine-grained segregations are spessartine grains; other segregations are rhodonite grains subjected to different degrees of supergene alteration.

brezhnaya and Tsentral'naya sutures. Hydrothermal activities in the Triassic and, possibly, Jurassic times were responsible for the delivery of a large amount of Mn, Fe, Sn, Zn, Pb, noble metals, and other elements to the marine basin. Ions of these metals were absorbed from hydrothermal solutions by clayey and organic materials of the radiolarian sediment. The transition of the noble metals and some other elements into the native state was fostered by severe reducing conditions of diagenesis and metamorphism.

Thus, we can draw the following conclusions. Metalliferous sediments are widespread in the Triassic– Jurassic carbonaceous sequence in the southern (Primorye) sector of Sikhote Alin. The four areas studied are located at a significant distance from each other and characterized by high concentrations of noble metals. Such metalliferous sediments can also be found in the northern sector. Results of the study of the Shirokaya Pad area suggest that the metalliferous sediments in other districts of Sikhote Alin may also contain very large reserves of Au, Ag, PGE, Sn, Zn, Pb, and other metals. We believe that the specific metallogenic feature of the southern sector of Sikhote Alin—presence of numerous Mn-rich skarn and vein deposits of Sn, Ag,

Pb, Zn, W, and Fe—is related to the extraction of these metals from the metalliferous sediments of the Triassic–Jurassic carbonaceous sequence.

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