*ISSN 1028-334X, Doklady Earth Sciences, 2006, Vol. 407A, No. 3, pp. 429–433. © Pleiades Publishing, Inc., 2006.*
*Original Russian Text © V.T. Kazachenko, N.V. Miroshnichenko, E.V. Perevoznikova, V.M. Chubarov, V.I. Kiselev, V.A. Solyanik, 2006, published in Doklady Akademii Nauk, 2006, Vol. 407, No. 4, pp. 516–520.*

**GEOCHEMISTRY**

# Gallium, Gold, and Platinum Group Metals in Manganese Rocks of Southern Sikhote Alin

**V. T. Kazachenko[1], N. V. Miroshnichenko[1], E. V. Perevoznikova[1], V. M. Chubarov[2], V. I. Kiselev[1], and V. A. Solyanik[1]**

Presented by Academician D. V. Rundqvist July 19, 2005

Received July 26, 2005

**DOI:** 10.1134/S1028334X06030184

In the Dal'nerechensk, Ol'ginsk, and Dal'negorsk ore districts of Sikhote Alin, the Triassic–Jurassic carbonaceous sequence includes metamorphosed metalliferous sediments [2, 3]. The upper, Jurassic part of the sequence is largely composed of carbonaceous mudstones and silty mudstones. The lower, Middle–Upper Triassic part consists of alternating carbon-rich siliceous and siliceous–clayey rocks. The carbonaceous sequence is intruded and metamorphosed by Late Cretaceous granitoids.

The metamorphosed siliceous and siliceous–clayey metalliferous sediments with rhodochrosite [2, 3] are confined to the lower part of the sequence. They are composed of rhodonite, pyroxmangite, and spessartine with a $V_2O_3$ content up to 8 wt %. Subordinate are kanoite, tephroite, manganactinolite, dannemorite, tirodite, pyrosmalite, pyrophanite, manganaxinite, helvite, bementite, barite, feldspars with a variable Ba content, Ba-phlogopite, phosphates with REE (monazite and apatite), native gold, sulfides, nickel and cobalt arsenides and sulfoarsenides, compounds of Bi, Pb, and Te, and other minerals. Rocks from different districts of the Primor'e region show both similarity and dissimilarity in mineral composition. For example, barite and feldspar are confined to metalliferous sediments of the Dal'nerechensk district.

Manganese rocks constitute conformable lenticular and stratiform bodies tens of centimeters to a few meters thick and tens to hundreds of kilometers long. Chains of such bodies form at the surface linear zones parallel to the strike of host rocks. Some zones are traceable owing to separate outcrops of 4.3 km (Ol'ginsk district) and 1.5–6.5 km (Dal'nerechensk district). In the Ol'ginsk district, the linear zones were partly regenerated into stockwork systems [1, 2]. The lenticular and stratiform bodies retained laminated structures complicated by small-scale folding.

According to the ICP-MS study, the metalliferous sediments are characterized, in contrast to the remaining part of the carbonaceous sequence, by the anomalously high content of Mn, Pb, Zn, Cu, Ba, V, Ga, Ta, Nb, Co, REE, and noble metals. Of particular interest are Ga, Au, Pt, and Pd, because their high concentrations suggest the presence of deposits of the new genetic type in Sikhote Alin. It is difficult to determine the concentrations of many elements in manganese rocks. The spectral analysis is ineffective because of the superimposition of Mn lines. The fire assay may result in losses because of insufficient melting (heaving and congealing of the melt on walls of the crucible), redox reactions, and other reasons. The atomic-absorption and ICP-MS methods require a special technique for sample decomposition. To avoid incorrect inferences, we determined Au contents by all methods mentioned above, except for the spectral one. The Ga, Pt, and Pd contents were determined only by the ICP-MS method using the equipment constructed by the Agilent Technologies, Inc., with acidic decomposition of samples. Au, Pd, and Pt reduced by tin chloride were concentrated by precipitation on elemental tellurium.

Ga is obtained from wastes of the processing of bauxites with a grade of ~50 ppm (95% of the world production) and Zn ores with similar or slightly higher contents. The Gold Canyon Resources Company is going to develop the unique Cordero deposit (United States), which has an average Ga content of 103.8 ppm [4]. The Ga contents range from *n* to 709.8 ppm in rocks of the Dal'nerechensk district (Table 1) and from *n* to 69.79 ppm in the Ol'ginsk district. Its average content is as high as 111.2 ppm in 18 samples from the

[1] *Far East Geological Institute, Far East Division, Russian Academy of Sciences, pr. Stoletiya Vladivostoka 159, Vladivostok, 690022 Russia; e-mail: vkazachenko@mail.ru*

[2] *Institute of Volcanology and Seismology, Far East Division, Russian Academy of Sciences, bul'v. Piipa 9, Petropavlovsk-Kamchatskii, 683006 Russia; e-mail: zond@kcs.iks.ru*

**Table 1.** Contents of Ga (ppm) and some other elements in manganese rocks of the southern Sikhote Alin

| Ord. no. | Sample no. | Ga | Ba | Zn | Ni | Co | Cu | As |
|---|---|---|---|---|---|---|---|---|
| Dal'nerechensk district | | | | | | | | |
| 1 | EV-01-54 | 26.3 | 395.8 | 202.3 | 35.54 | 23.9 | 44.6 | 30.35 |
| 2 | EV-01-22 | 2.432 | 29.04 | 116 | 36.27 | 25.77 | 7.019 | 22.01 |
| 3 | EV-01-13 | 37.97 | 641.2 | 169.5 | 359.4 | 89.9 | 28.97 | 771.9 |
| 4 | EV-93-507 | 6.17 | 90.87 | 162.1 | 90.6 | 60.98 | 4.668 | 44.7 |
| 5 | EV-04-5 | 65.39 | 2172 | 1549 | 524.5 | 341.7 | 13.72 | 1231 |
| 6 | EV-04-6 | 19.76 | 293.9 | 152.7 | 134.3 | 79.62 | 44.38 | 161.5 |
| 7 | EV-04-11 | 709.8 | 10730 | 525.1 | 295.7 | 108.5 | 38.67 | 130.8 |
| 8 | EV-04-18 | 65.47 | 2053 | 597.5 | 128.6 | 596.1 | 13.23 | 236.5 |
| 9 | EV-04-12 | 74.89 | 2099 | 123.4 | 46.6 | 61.68 | 15.3 | 37.59 |
| 10 | EV-93-511 | 53.1 | 879.3 | 389.2 | 277.9 | 263.2 | 11.37 | 330.3 |
| 11 | EV-04-17 | 54.25 | 893.6 | 396.8 | 287.2 | 269.8 | 11.65 | 334.2 |
| 12 | EV-04-16 | 45.71 | 692.4 | 616 | 158 | 499.5 | 6.347 | 49.41 |
| 13 | EV-04-4 | 20.8 | 342.5 | 5502 | 1331 | 198.3 | 11.37 | 792.8 |
| 14 | EV-93-512 | 5.316 | 67.43 | 332.3 | 219.4 | 198.8 | 5.99 | 157.8 |
| 15 | EV-04-1 | 227.6 | 2973 | 421.7 | 575.3 | 245.9 | 131.6 | 380.8 |
| 16 | EV-01-55 | 282.2 | 3.73 | 244.5 | 51.06 | 72.79 | 59.22 | 67.93 |
| 17 | EV-01-45 | 301.6 | 4.147 | 289.4 | 101.5 | 90.68 | 55.14 | 94.37 |
| 18 | EV-01-22 | 2.812 | 37 | 233.8 | 39.02 | 30.62 | 22 | 21.84 |
| 19 | Average | 111.20 | 1355.44 | 667.96 | 260.66 | 180.99 | 29.18 | 271.99 |
| Ol'ginsk district | | | | | | | | |
| 21 | K-80-13 | 6.09 | 64.2 | 59680 | 270 | 328 | 6372 | 124 |
| 22 | Sh-80-10 | 37.31 | 846.7 | 1191 | 144.2 | 72.35 | 32.89 | 63.94 |
| 23 | K-80-14 | 4.696 | 39.73 | 532.7 | 262.6 | 1021 | 35.2 | 599.7 |
| 24 | R-80-39 | 10.31 | 113.8 | 407 | 65.57 | 114.7 | 643.1 | 512.7 |
| 25 | MT-81-15/17 | 69.79 | 2377 | 7863 | 274 | 395.8 | 297 | 304.7 |
| 26 | F-04-2 | 1.619 | 19.95 | 909.8 | 528.1 | 342.1 | 65.63 | 11.2 |
| 27 | Sh-86-183 | 20.52 | 276.4 | 286.5 | 55.41 | 198 | 22.26 | 117.8 |
| 28 | Sh-86-97 | 28.54 | 438.9 | 262.7 | 83.48 | 108.8 | 851.6 | 73.6 |
| 29 | Sh-86-41 | 2.114 | 23.13 | 1483 | 39.06 | 30.32 | 53.13 | 20 |
| 30 | F-04-2a | 1.539 | 17.11 | 1627 | 1377 | 525.8 | 53.8 | 24.72 |
| 31 | F-04-3 | 2.922 | 22.47 | 1391 | 149.4 | 335.8 | 36.67 | 186.3 |
| 32 | F-04-1 | 6.165 | 94.92 | 1736 | 76.57 | 50.55 | 76.47 | 83.07 |
| 33 | F-04-4a | 3.036 | 35.22 | 5817 | 109.3 | 39.51 | 15.73 | 104.2 |
| 34 | Average | 14.973 | 336.118 | 6398.977 | 264.207 | 274.056 | 658.114 | 171.225 |

Dal'nerechensk district and 14.973 ppm in 13 samples from the Ol'ginsk district. Sample EV-04-11, with the highest Ga content, yielded the maximal Ba concentration as well (>1 wt %). The Ga content in manganese rocks grows with an increase in Ba concentrations. Therefore, one can suggest that Ga is incorporated into the structure of feldspars and micas.

The Au content first determined in manganese rocks of the Ol'ginsk district by the atomic absorption method without extraction from solution was estimated at 5–40 g/t (Table 2). We dissolved 15 samples (up to 100 g each) in order to test these results and specify mineral phases of Au (D.T. Presich, analyst). The content of native Au varied from 1 to 64 grains in 13 samples. Their dimensions vary from a few tens to hundreds of a millimeter. Large grains are equant, while small grains are platy. Grains are yellow to, rarely, pale yellow (almost white) in color. The size, color, and composition change even in the same sample. Native Au is usually very pure: the ratio of the Au content and

**Table 2.** Contents of Au, Pt, and Pd (g/t) in manganese rocks of the southern Sikhote Alin

| Ord. no. | Sample no. | Au, fa | Au, a | Au, a' | Au, a" | Au I | Pd I | Pt I |
|---|---|---|---|---|---|---|---|---|
| Dal'nerechensk district | | | | | | | | |
| 1 | EV-04-1 | **0.18** | | | | **0.2497** | 0.001693 | **0.2826** |
| 2 | EV-04-4 | 0.06 | | | | 0.004459 | **0.1024** | **0.7015** |
| 3 | EV-04-5 | 0.05 | | | | 0.001619 | 0.01004 | 0.005197 |
| 4 | EV-04-6 | 0.05 | | | | ≤0.0001 | 0.002139 | 0.002652 |
| 5 | EV-04-11 | 0.02 | | | | 0.001994 | 0.002778 | 0.001208 |
| 6 | EV-04-12 | **0.12** | | | | ≤0.0001 | 0.003515 | 0.0005217 |
| 7 | EV-04-16 | 0.01 | | | | 0.0003264 | **0.1246** | **1.542** |
| 8 | EV-04-17 | 0.02 | | | | 0.03264 | ≤0.0001 | 0.001338 |
| 9 | EV-04-18 | **0.10** | | | | ≤0.0001 | 0.00699 | 0.01398 |
| 10 | EV-01-13 | **3.06** | | | | | | |
| 11 | | **0.80** | | | | 0.005525 | **0.13** | 0.02809 |
| 12 | EV-01-22 | 0.05 | | 4.4261 | | 0.006387 | 0.003999 | 0.009748 |
| 13 | EV-01-45 | 0.04 | | | | 0.04703 | **5.333** | **1.222** |
| 14 | EV-01-54 | 0.04 | | | | 0.01042 | 0.0001312 | 0.01371 |
| 15 | EV-01-55 | 0.01 | | | | **0.1602** | 0.05154 | **0.6567** |
| 16 | EV-93-507 | 0.02 | | 5.169 | | 0.005208 | **0.2271** | 0.037772 |
| 17 | EV-93-511 | 0.04 | | 3.2121 | | ≤0.0001 | 0.001278 | 0.009447 |
| 18 | EV-93-512 | **1.17** | | | | **8.432** | 0.004843 | **1.294** |
| 19 | | 0.01 | | | | | | |
| 20 | EV-93-504 | | | 1.783 | | | | |
| 21 | EV-93-516 | | | 3.0071 | | | | |
| Ol'ginsk district | | | | | | | | |
| 22 | F-04-2 | 0.03 | | | | 0.007405 | 0.006441 | **0.113** |
| 23 | F-04-2‡ | 0.04 | | | | 0.004833 | 0.007425 | 0.01785 |
| 24 | F-04-3 | 0.01 | | | | 0.0026671 | 0.01491 | **0.142** |
| 25 | F-04-1 | **35.38** | | | | | | |
| 26 | | 0.02 | | | | 0.005015 | ≤0.0001 | **0.125** |
| 27 | F-04-4a | 0.08 | | | | 0.002096 | 0.0003115 | 0.085 |
| 28 | Sh-86-41* | 0.02 | | | | 0.003551 | ≤0.0001 | **0.31** |
| 29 | Sh-86-97 | 0.01 | | | | 0.007529 | 0.004515 | 0.01897 |
| 30 | Sh-86-183 | 0.07 | | | | 0.01055 | 0.00499 | **0.138** |
| 31 | K-80-14 | 0.02 | 10 | | | 0.02269 | 0.004556 | **0.33** |
| 32 | R-80-39 | 0.01 | | | | 0.01908 | 0.003409 | 0.083 |
| 33 | MT-81-15 | 0.02 | | | | 0.008879 | 0.002286 | 0.01437 |
| 34 | B-79-102 | | 25 | | | | | |
| 35 | Sh-80-2 | | 10 | | | | | |
| 36 | Sh-80-1 | | 5 | | | | | |
| 37 | R-80-4 | | 15 | | | | | |
| 38 | R-80-19* | | 40 | | | | | |
| 39 | R-80-41 | | 25 | | | | | |
| 40 | R-80-8* | **0.12** | 12.5 | 1.1466 | | | | |
| 41 | R-80-42 | | 20 | | | | | |
| 42 | K-80-21 | | 7.5 | | | | | |
| 43 | Sh-80-7 | | 27.5 | | | | | |
| 44 | K-80-1 | | 7.5 | | | | | |
| 45 | K-80-11 | 0.06 | | 0.9927 | | | | |
| 46 | K-80-13* | **0.17** | | 1.5468 | 0.010 | 0.0322 | 0.009268 | 0.01359 |
| 47 | R-80-18 | 0.05 | | 1.7315 | | | | |
| 48 | K-80-20 | **0.11** | | 2.9320 | | | | |
| 49 | K-80-10 | | | | 0.0068 | 0.06758 | 0.03986 | 0.04496 |

Note: (Au, fa) fire assay (Laboratory for the Analysis of Noble Metals, Far East Geological Institute, Vladivostok); (Au, a) atomic absorption analysis (without extraction) (analyst V.F. Bakilina, Far East Geological Institute); (Au, a') atomic absorption analysis (with extraction by butyl sulfide) (Analytical Laboratory of Noble Metals, Far East Geological Institute); (Au, a") atomic absorption analysis (Analytical Center of the United Institute of Geology, Geophysics, and Mineralogy, Novosibirsk, analysts V.G. Tsymbalist and G.I. Ornatskaya); (Au I, Pd I, Pt I) ICP-MS analysis (Laboratory of Analytical Chemistry, Far East Geological Institute); Asterisk denotes samples that yielded native gold in the course of dissolution. Bold numbers designate elevated and high contents based on the fire assay and ICP-MS data.

**Table 3.** Composition of native gold from manganese rocks of the Ol'ginsk ore district

| Sample no. | Grain | Au | Ag | Sum | Fineness | Size, color |
|---|---|---|---|---|---|---|
| R-80-19 | 1 | 87.05 | 13.60 | 100.65 | 865 | Very small, yellow |
| | 2 | 88.90 | 12.30 | 101.20 | 878 | The same |
| R-80-41 | 1 | 71.94 | 27.40 | 99.34 | 724 | Small, yellow |
| | 2 | 67.90 | 29.99 | 97.89 | 694 | The same |
| | 3 (a) | 99.62 | 0.00 | 99.62 | 1000 | " |
| | 3 (b) | 80.14 | 19.03 | 99.17 | 808 | " |
| | 4 | 70.35 | 29.56 | 99.91 | 704 | " |
| | 5 | 67.51 | 32.91 | 100.42 | 672 | " |
| | 6 | 98.77 | 1.31 | 100.08 | 987 | " |
| | 7 | 62.84 | 36.89 | 99.73 | 630 | " |
| | 8 | 88.37 | 11.79 | 100.16 | 882 | " |
| | 9 | 87.41 | 12.22 | 99.63 | 877 | Very small, yellow |
| | 10 | 76.50 | 23.45 | 99.95 | 765 | The same |
| | 11 | 80.72 | 18.31 | 99.03 | 815 | " |
| | 12 | 88.00 | 11.95 | 99.95 | 880 | " |
| | 13 | 54.21 | 46.83 | 101.08 | 536 | Very small, pale yellow (almost white) |

Note: The composition is determined using a JXA-5A electron microprobe in the Far East Geological Institute, Vladivostok (V.I. Sapin, analyst).

sum of noble metals (reduced to 100%) is 790 (Table 3). This ratio is 71.7 in rocks (average for 12 samples analyzed by the atomic absorption method). Therefore, one can assume that almost whole Au and Ag are present in the form of solid solution. According to fire assay data on two samples analyzed in the Primor'e Geological Survey, the Au content varied from 0.2 to 0.3 g/t. The atomic absorption analysis of one sample with extraction of Au by petroleum sulfides (V.F. Bakilina, analyst) showed negative results, which served as a ground for stopping studies.

Later on, microprobe studies demonstrated that ore minerals from manganese rocks of the Dal'nerechensk district contain up to 1500 g/t of Au. However, such contents seemed doubtful and could be related to incorrect determination of background values in the sample. Further studies revealed a gold grain approximately 1.5 μm across in one of the polished samples. According to the microprobe analysis (Camebax; Institute of Volcanology and Seismology, Petropavlovsk-Kamchatskii; V.M. Chubarov, analyst), the grain contains Au (62.60 wt %), Mn (6.06 wt %), Cu (0.74%), and Ni (0.01 wt %). The presence of Mn and deficiency of the total sum are explained by the insufficient grain size.

Therefore, we continued to study the geochemistry of gold in rocks of the Ol'ginsk district. Samples of heavy fractions were dissolved in hydrofluoric acid (N.A. Vasil'tsova, analyst). Although only 20–30 vol % of the fraction were dissolved, four of 14 samples yielded 1–3 gold grains 0.*n* mm across. The atomic absorption method with Au extraction by dibutyl sulfide was used to analyze gold from the Ol'ginsk and Dal'nerechensk districts (five samples each, including two samples extracted by dissolution from the Ol'ginsk district). The results show that the Au content ranges from 0.9927 to 2.9320 g/t in the Ol'ginsk district and from 1.783 to 5.169 g/t in the Dal'nerechensk district (Table 2). Among two samples from the Ol'ginsk district analyzed by the atomic absorption method at the United Institute of Geology and Geophysics in Novosibirsk, one sample yielded native Au.

Because of conflicting results, the Au content was determined by the fire assay and ICP-MS methods in the same samples from the Ol'ginsk and Dal'nerechensk districts. These studies confirmed the presence of a negligible amount of Au in some samples from both districts (Table 2). Pt and Pd contents were determined by the ICP-MS method. It appeared that 28–33% of samples from the Dal'nerechensk district are characterized by elevated (0.*n* g/t) or high contents of Pt and Pd; 17% of samples showed high Au concentrations (Table 2). The high contents are more characteristic of Pt, whereas Au and Pd show usually elevated contents. Moreover, the latter statement is valid for samples with high or elevated Pt concentrations. The high Au and Pd contents are only typical of samples with high Pt concentrations. Au and Pd practically never occur together. Thus, pairs Au–Pt and Pt–Pd are in close geochemical relations. Almost all samples with elevated or high Pt, Pd, and Au contents are also characterized by anomalously high concentrations of other elements, combinations of which are variable in samples. Most typical of them are Zn, Ni, Ba, Ga, and Co, which are sometimes accompanied by As and Cu (Table 1). Taking into consideration the results of microprobe studies, it can be assumed that Pt, Pd, and Au associate in different forms with sulfides, arsenides, and sulfoarsenides of Ni and Co, sphalerite, chalcopyrite, and compounds of Te and Bi.

The comparison of data obtained for the rocks from the Dal'nerechensk district (Table 2) shows that the ICP-MS and fire assay methods provided comparable Au contents in two of three samples, with Au concentrations ranging from 0.*n* to *n* g/t. In sample EV-01-55, the ICP-MS method revealed also Pt, in addition to Au, which was probably lost during its study by the fire assay. Of six samples, which yielded similar Au contents, when analyzed by the fire assay, only two showed presence of Au under the ICP-MS treatment. This seems natural, when differences in sample weights (50 times) combined with the irregular Au distribution in rocks are taken into account. Discrepancies in results of parallel analyses (18 and 19, 25 and 26) by the fire assay can be explained by Au losses. The elevated and high contents of noble metals were established by the fire assay or ICP-MS method in almost 60% of samples from this district.

The manganese rocks from the Ol'ginsk district are described in [1, 2]. In the Dal'nerechensk district, they occur at the same stratigraphic level within a sequence and are similar in mineralogy, associations, and composition. Their association with Triassic–Jurassic carbonaceous rocks, which are widespread in Sikhote Alin, points to the formation of metalliferous sediments in a marginal sea basin. This inference is also supported by the bivalent form of Mn, high Mn/Fe value, and relatively low Ni, Co, and Cu contents. By these features, they are close to sediments accumulated near continents [5]. Similar to host rocks, the metalliferous sediments are enriched in the same elements (Ba, V, Cu, Zn, Pb, Ni, Co, Ga, and others), but to a higher degree. Hence, the sediments are products of diagenetic or hydrothermal–sedimentary (when host rocks were leached) processes.

Reaction between carbonate, siliceous, and clayey materials in the course of metamorphism produced various manganese silicates and aluminosilicates. Temperature parameters of metamorphism (490–560°C and 250–500°C for the Dal'nerechensk and Ol'ginsk districts, respectively) [1, 3] are consistent with their geological positions. In terms of redox conditions, rocks of the Ol'ginsk district belong to fayalite and quartz–magnetite subfacies of the manganosite–magnetite facies [1], whereas rocks of the Dal'nerechensk district belong to the fayalite subfacies. Reducing environments are explained by the high content of organic matter in primary sediments.

Thus, the manganese rocks, include the varieties discussed above, deserve particular attention because they may enclose Ga–Au–Pd–Pt deposits of the new genetic type. The study of such objects requires furrow sampling. In order to avoid losses of noble metals during fire assay, atomic absorption, and ICP-MS analyses, special melting and chemical decomposition techniques are recommended.

## ACKNOWLEDGMENTS

This work was supported by the Presidium of the Far East Division of the Russian Academy of Sciences, project no. 05-1-onz-10A.

## REFERENCES

1. V. T. Kazachenko, *Petrology and Mineralogy of Hydrothermal Manganese Rocks of Eastern Russia* (Dal'nauka, Vladivostok, 2002) [in Russian].
2. V. T. Kazachenko and V. I. Sapin, *Mineralogy and Genesis of Fe–Mn Mineralization of the Primor'e Coastal Zone* (Vladivostok, 1990) [in Russian].
3. V. T. Kazachenko, V. M. Chubarov, V. A. Solyanik, and G. A. Narnov, Dokl. Akad. Nauk. **400**, 785 (2005) [Dokl. Earth Sci. **401**, 232 (2005)].
4. *Metal Bulletin Monthly* (2002).
5. S. Roy, *Manganese Deposits* (Academic Press, London, 1981; Mir, Moscow, 1986).