Noble metals in rocks and ores of Maysko–Lebed ore field (Mountain Shoriya)

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Abstract. First the authors determined platinum and palladium in the ores and rocks of Maysk–Lebed ore deposit via stripping voltammetry. Based on research data the increased platinoid (platinum group elements) content was identified both in the source host rocks and in metasomatically altered ones in ores.

1. Introduction
Currently, integrated study on platinum group elements in gold -ore and other deposits is considered to be of significant importance, due to two major aspects: on the one hand, conventional noble metal deposit depletion, while, on the other hand, the majority of different genetic deposits embrace high platinoid concentration (including even commercial reserves) [1].

The authors performed an integrated study on Pt, Pd and Au concentrations in the rocks and ores of Maysk–Lebed ore field via stripping voltammetry within the Gold–Platinum Research and Education Innovation Center, Tomsk Polytechnic University. The preliminary study results showed a high concentrations of Pt and Pd not only in source host rocks but also in near-ore metasomatites and ores.

The source material included rock and ore samples collected during the theme-based research (2004-2008), detailed mineral and geochemistry mapping of available mine openings, and drill hole cores from drill core samples from Maysk–Lebed ore deposit. The study group included the employees of the Department of Geology and Minerals Exploration, Tomsk Polytechnic University in collaboration with personnel of Tetis-T LLC (Novokuznetsk, Russia) [2].

2. Geological Setting
Maysk–Lebedev gold-ore field is located in North–East Gorny Altai of North Altai gold bearing zone within the near north-south strike intersection of Kuznetsk Alatau and near EW -Western Sayan within Altay–Kuznetsk–Western–Sayan volcano–plutonic belt. Such a location could be explained by the continuous ore field formation history involving a succession of tectonic–magmatic impulses and hydrothermal activity [3, 4, 5].

The Maysk–Lebed ore field development embraced Maysk, Magalaksk and Chanysk intrusive massif of the Sardinsk complex. Two rock groups were identified in the massif: gabbro, gabbro-diorites and granodiorites, quartz diorites. This massif formed during two stages: initial-gabbrodiorite and final -granitoid. Granodiorites are regional throughout the inner massif, while quartz diorites are in endomorphosed massif zone. As a result of hydrothermal–metasomatic transformations of rocks, skarns, propylites, beresites with veinlet silicification and argillizated rocks developed.

The ore field area has a block structure. Such blocks are usually isolated by tectonic wedges and characterized by thrust-faults and strike–slip faults. The principal ore controlling structure embraces N-S strike small-scale faults and anticline fold hinges. The combination of such structures is
considered to be the most favorable ones for mineralization. N-W faults are predominately post-ores and do not significantly influence the ore localization itself.

Two heterochronous geological and industrial types of ore grade mineralization have been identified in the Maysk–Lebed ore field: contact–metasomatic deposits of gold–magnetite–sulfide ores in Caledonian aposkarn propylites (Maysk area) and mineralized zones of Hercynian gold–sulfide–quartz vein–disseminated ores accompanied by the beresitization of host rocks (Pravoberezhny and Semenov areas).

Maysk gold–skarn ore bodies are localized in the eastern exocontact of Maysk granodiorite–diorite intrusive massif within thick skarnified and quartz–epidote–chlorite and quartz–sercite–carbonate metasomatite zone. The basic ore mineralization includes pyrite, magnetite, chalcopyrite and gold, as well as rare minerals – pyrrhotine and cobaltite.

Pravoberezhny and Semenov ore bodies are localized in the Lower Cambrian igneous rocks (Sardinsk suite) and include gold–sulfide–quartz lenses of 0.1–0.7 m thickness, accompanied by sulfidized beresites of 10–15 m thickness. Ore mineralization includes pyrite, arsenopyrite, chalcopyrite, galena, tetrahedrite and gold.

Hierarchical three–level ore–metasomatic zoning was defined for the Maysk–Lebed ore field [4, 6]: ore field, ore deposit and ore body. Identified cross–section zoning in all three levels is characterized as concentric convergent and three detected zones within the ore–bearing structures. In the central zone, near–ore metasomatites with gold–magnetite–sulfide and gold–magnetite–quartz mineralization are well-developed. The intermediate zone is characterized by propylites with pyrite–arsenopyrite mineralization. The external zone, showed dispersed pyrite mineralization. Cross–section zoning is governed by the structural conditions of localized ore mineralization and reflects the differentiated character of geological structure permeability. Axial ore field zoning was identified on the cross–section zoning background which was revealed in the ore deposition temperature decrease from south (Maysk area) to the north progressively in a direction away from the ore–generating intrusive bodies (Pravoberezhny and Semenov areas). Within the ore field the zoning itself reveals the regular changing of high–temperature metasomatites (skarns) to low–temperature metasomatites (beresites, argillitized rocks), regular assay of gold reduction (from 600 to 980 %), increasing Ag/Au ratio (from 1:1 to 10:1) in ores and alteration of typomorphic pyrite and metasomatite mineral properties.

3. Research Methods

The high–sensitive and economical method – stripping voltammetry (SV) – was applied in analyzing rocks and ores of the Maysk–Lebed ore field to assay the Pd, Pt and Au content. The evaluation of the platinum metal and gold content via SV method has been applied by the personnel of the Gold–Platinum Research and Education Innovation Center, Tomsk Polytechnic University [7,8].

The SV method eliminates the numerous interfering base (trace) components in a sample by selecting that platinoid electrodeposition potential where the base components electroconcentration would be excluded. Therefore, the total saline background system with such elements as Na, K, Cr, Pb, Mn and others does not interfere in the identification of platinoids. However, such elements as Cu, Fe, Se, Te that oxidize under positive potentials may interfere in the SV identification of these platinoids. At the same time, a mutual influence of noble elements is observed. To identify platinum group metals and gold by the SV method, analysis outlines are designed to provide either the isolation of base (trace) components or the precipitation of single platinum group metals.

The isolation and identification of Pd, Pt and Au involve a multi–stage process. Initially, "dry" oxidation of samples is performed at 750 °C for 45 minutes. Then, the annealed samples are treated by a concentrated acid mixture ("moist" oxidation) for further deposition of some metals in solution.

To isolate palladium (II) from the solutions after the deposition of analyzed ore sample in solution, dimethylglyoxime Pd(II) extraction complex with chloroform is applied; to isolate gold (III) chloride Au(III) extraction complex with diethyl ether is applied. Identification of platinum (IV) in samples was performed after sample matrix isolation via deposition method with bromate hydrolysis.
Measurement technique for gold and palladium weight concentration is based on stripping voltammetry analysis of sample solution after its preliminary treatment. Gold and palladium electrolytic deposits settle on the surface of a graphite electrode from chloride gold (III) and palladium (II) solutions.

Identification of platinum (II and IV) in solutions by stripping voltammetry analysis is possible only with electro-negative metal settled on graphite electrode surface and further selective electro-oxidation of alloy [7,8]. Indium is used as an electro-negative metal.

TA–4 voltampermetry analyzer (produced by TomAnalit LLC Tomsk, Russia) was applied in the research. All measurements were performed in three–electrode cell with main graphite low–pressure polyethylene impregnated electrode. Saturated chloride–silver electrode was used as reference and auxiliary electrode, respectively. Deaeration of solutions was not performed.

Stripping voltammetry analysis with graphite electrode identifies the platinum group elements and gold within an interval of 10^{-8}–10^{-2} wt % on weight of 1–5 grams. Element identification accuracy was evaluated by the correlation of reference sample results to parallel line sample analysis (the latter by atom absorption spectroscopy).

### 4. Research Results and Discussion

The stripping analysis voltammetry was used to assay platinum, palladium and gold in samples of 123 host rock, near–ore metasomatites and ores of Maysk and Pravoberezhny deposits. First determined rather high platinum and palladium content both in unaltered host rocks (tuffs, andesites) and in skarns, near–ore metasomatites and ores (table 1).

#### Table 1 Gold, platinum and palladium content in rocks and ores of Maysk–Lebed ore field

| Rocks and ores          | n  | Gold, g/t | Platinum, mg/t | Palladium, mg/t |
|-------------------------|----|-----------|----------------|-----------------|
|                         |    | from      | to X           | from to X       |
| Andesite tuff           | 3  | 0.033     | 0.20 0.081 0.73 0.10 0.10 | 0.14 0.61 |
| Scarnified andesite tuff| 12.0 | 0.11     | 8.30 2.05 6.5 50.5 26.7 1.0 45.0 10.7 |
| Limonitized andesite tuff| 19.0 | 0.40     | 9.40 1.19 1.9 50.5 23.4 1.0 48.0 8.7 |
| Andesite                | 4.0 | 0.23      | 1.10 0.69 4.4 21.2 10.8 6.0 33.0 19.0 |
| Scarnified andesite     | 10 | 0.60      | 4.70 2.48 5.9 94.4 31.8 1.0 4.8 2.3 |
| Limonitized andesite    | 8.0 | 0.72      | 12.0 4.45 1.2 47.6 16.2 7.2 32.0 15.5 |
| Garnet–epidote skarn    | 4.0 | 0.15      | 0.99 0.57 5.5 30.8 12.2 8.1 75.0 26.7 |
| Ore                     | 13.0 | 0.20    | 22.2 5.92 2.1 55.5 20.2 1.0 86.0 30.0 |
| Propylite               | 6.0 | 0.011     | 6.10 2.10 1.0 50.0 15.2 1.0 12.5 4.1 |
| Magnetite               | 3  | 0.02      | 0.12 0.07 2.1 8.1 4.0 1.0 9.3 3.6 |

#### Pravoberezhny area

| Rocks and ores          | n  | Gold, g/t | Platinum, mg/t | Palladium, mg/t |
|-------------------------|----|-----------|----------------|-----------------|
|                         |    | from      | to X           | from to X       |
| Andesite tuff           | 6.0 | 1.00     | 2.60 1.75 5.7 42.9 16.2 1.1 61.0 17.4 |
| Scarnified andesite tuff| 2.0 | 0.17     | 0.23 0.20 21.1 23.4 22.3 7.9 9.5 8.7 |
| Limonitized andesite tuff| 3.0 | 0.23    | 0.84 0.49 2.8 21.1 10.6 9.5 66.0 31.7 |
| Andesite                | 5.0 | 0.10     | 4.40 1.40 5.7 32.8 18.2 1.8 32.0 13.2 |
| Limonitized andesite    | 3.0 | 0.51     | 1.50 0.95 3.0 60.1 28.8 1.0 67.0 23.3 |
| Beresite                | 7.0 | 0.31     | 3.00 1.00 4.2 58.3 22.5 1.0 240.0 49.4 |
| Ore                     | 8.0 | 0.23     | 5.30 2.46 3.2 50.1 19.3 1.0 130.0 27.0 |
| Ironstone               | 4.0 | 1.00     | 7.00 2.90 9.9 34.5 19.7 2.0 93.0 42.4 |
| Calcite veinlet in beresites| 1.0 |       | 0.072 – – 20.8 – – 0.41 |
| Quartzite               | 1.0 |       | 0.091 – – 6.7 – – 38.0 |
NB: n – number of analyses; X – average value; analyses performed in Gold–Platinum Research and Education Innovation Center, TPU (by analytical chemists: E Gorchakov – Au; Yu Oskina – Pd; E Ustinova – Pt).

Platinum. Platinum content scatter in Maysk area is from 1.0 mg/t (andesite tuffs, propylites) to 94.4 mg/t - scarnified andesites. The latter (scarnified andesites) has highest average platinum content of 31.8 mg/t. Normal average platinum concentrations were defined in the ores (20.0 mg/t), limonitized (23.4 mg/t) and scarnified (26.7 mg/t) tuffs. Platinum content is half as high in unaltered andesites (10.8 mg/t) and in garnet–epidote barren skarns (12.2 mg/t). Lowest average platinum concentration was found in unaltered andesite tuffs (3.4 mg/t) and in magnetites (4.0 mg/t).

Rather normal platinum concentrations -16.2–22.3 mg/t with content scatter from 2.8 (limonitized tuffs) to 60.1 mg/t (limonitized andesites) have been observed in the rocks and ores of the Pravoberezhny area, whereas the highest average concentrations were also observed (28.8 mg/t). Limonitized tuffs are less platinum concentrated – 10.8 mg/t.

Palladium. Palladium concentration varies from 1.0 mg/t (in most rocks and ores) to 75.0 and 86.0 mg/t (in garnet–epidote skarns and ores) in the Maysk area; whereas in the latter, the highest and normal average palladium concentration (26.7 and 30.0 mg/t) was observed. The highest and normal average palladium concentration was defined in unaltered (19.0 mg/t) and limonitized (15.5 mg/t) andesites. Ther lowest average platinum concentration was observed in scarnified andesites, magnetites and propylite (2.8, 3.6 and 4.1 mg/t, respectively).

A higher palladium concentration was observed in most rocks and ores of the Pravoberezhny area in comparison to those in the Maysk area where content scatter is from 1.0 mg/t (beresites, ores, ironstone) to 130.0 and 240.0 mg/t (ore quartz and beresites). The highest average palladium concentration has been observed in beresites (49.4 mg/t), ironstones (42.4 mg/t) and a bit lower in limonitized tuffs (31.7 mg/t) and in ore quartz (27.0 mg/t). The lowest average concentration was observed in scarnified tuffs (8.7 mg/t) and unaltered andesites (13.2 mg/t). In a single sample from a, the lowest palladium concentration (0.41 mg/t) was observed in one veinlet calcite sample of beresites for this ore field.

A platinum and palladium concentration decrease in dependence with depth of scarnified andesites and propylites was also observed in the Maysk area.

Gold. Gold concentration in the rocks and ores of the Maysk area vary from 0.011 g/t (propylites) to 22.0 g/t (ores), whereas the highest average gold concentration was observed in the ores (5.92 g/t) and limonitized andesites (4.45 g/t). Normal average gold concentration could be observed in propylites (2.1 g/t), tuffs (2.05 g/t) and scarnified andesites (2.48 g/t). The lowest average gold concentration was observed in unaltered andesite tuffs (0.081 g/t) and magnetites (0.07 g/t). An average metal content increase was observed in andesite (0.69) – scarnified andesite (2.48) – limonitized andesite (4.45 g/t). (table 1).

The gold concentration is a bit lower in most rocks and ores of the Pravoberezhny area in comparison to those in the Maysk (table 1), whereas the content scatter is even less – from 0.1 g/t (andesite) to 7.0 g/t (ironstone). The highest average gold concentration has been observed in the ores and ironstones (2.46 and 2.9 g/t). Normal average gold concentration was found in andesite tuffs (1.75), andesites (1.4), beresites (1.0) and limonitized andesites (0.95 g/t). Scarnified and limonitized tuffs contain low–grade gold (0.2 and 0.49 g/t, respectively). Single gold concentrations were observed in quartzites and post-ore veinlet calcite in the beresites of the Pravoberezhny area - lowest concentration (0.091 and 0.072 g/t, respectively).

5. Conclusion
1. Highest platinum and palladium concentrations have been found in the ores of Maysk–Lebed deposit and normal average concentrations in the Maysk and Pravoberezhny areas.
2. During skarnification and supergene formation (limonitizing) of rocks and ores, metal re-distribution and even their increase, in some cases, was observed.
3. Gold concentration level in the rocks and ores of the Maysk area is higher than of those in the Pravoberezhny area.

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