# FEATURES OF OCCURRENCE AND DISTRIBUTION OF NOBLE METALS IN THE ORES AND OXIDIZED ZONE OF THE ONEGA URANIUM–VANADIUM DEPOSITS, SOUTH KARELIA

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Complex uranium-vanadium ores with Mo, Cu, Bi and Pb from the Onega deposits, which contain large reserves of vanadium and probably noble metals (Pd, Au, Ag, Pt), are limited by near-surface and deep-seated bedded oxidized zones. In addition, deep joint oxidized zone and hydrothermal roscoelite – chromceladonite – dolomite veinlets occur at the deposits. The highest contents (much higher than 10 ppm) of noble metals have been identified in these veinlets. Minerals of noble metals are native gold, selenides, less frequent selenide-sulfides, tellurides, and compounds with bismuth, lead, and other elements. Redeposited native copper, auricupride, native platinum, froodite, isoferoplatinum, palladium analogue of auricupride, the new natural phase, and the phase AuO(OH) have been identified in the oxidized zones with the highest contents of noble metals. Gold segregations from the near-surface oxidized zone of low noble-metal content (lower than 10 ppm) are fine clusters up to 0.1 μm in size. In the upper part of the deep-seated oxidized zone, gold occurs as broken spindle-shaped 2-3 μm particles. Close to the intermediate part of the deep-seated oxidized zone, gold crystals are disseminated in blades of native copper that reach several tens of μm in size.

The results obtained confirm previous assumption on the probable increase in noble-metal reserves adjacent to explored uranium-vanadium deposits.

4 tables, 6 figures, 16 references.

The Onega U-V deposits with noble metals (Pd, Pt, Au, Ag), Mo, Cu and Bi are rich in vanadium reserves and these probably contain associated noble metals. Assumption of large reserves of noble metals was supported the previous studies that found significant concentrations of Pd, Pt, Au, and Ag adjacent to the U-V ores (Chernikov, 1997, 2001; Chernikov *et al.*, 2000).

The Srednyaya Padma, Tsarevskoe, and Kosmozero deposits occur at the contact with grayish red-brown (hematitized) Lower Proterozoic dolomites (Bilibina *et al.*, 1991; Laverov *et al.*, 1992; Mel'nikov *et al.*, 1992, 1993, 1995; Ledeneva & Pakul'nis, 1997) of the ancient deep-seated bedded oxidized zone (Poluektov *et al.*, 1998; Chernikov *et al.*, 2000; Chernikov, 2001) in the Onega riftogenic basin located in the southeastern Baltic Shield.

The U-V ores of the Onega deposits are different mineralogical types with distinct mineralogical and geochemical zoning. A low-temperature sodium metasomatic rock (albitite) occurs at the margins of the ore deposits at the furthest distance from the boundary with the deep-seated oxidized zone; the U-V mineralization with Cu-Mo sulfides overprints the inner part of this metasomatic zone. The Cu-Mo uranium-vanadium ore is followed by the V-rich chromceladonite-roscoelite zone alternating with ordinary U-V ore with the areas enriched in uranium and noble metals. The U-V ore is bounded by the hematitized dolomites. The zoning of the mineral assemblages is identified at each deposit of the district. Calcite and hematite veinlets and breaks formed as a result of deep joints in the oxidized zone and cross-cut all of the above mineral assemblages. They cut both orebodies and hematitized dolomites. Nevertheless, the hydrated uranium oxides (Fig. 1) are observed in all mineral assemblages. The boundary of the deep-seated bedded oxidized zone (Fig. 2) is the clear oxidized-reduction barrier and plays a major role in forming the complex ores. The near-surface modern oxidized zone with abundant brown and dark-brown iron and manganese oxides is the upper boundary of the U-V ore at all deposits down to 30 m (less frequent 150 m) below the surface (Fig. 2).

Dolomites near the contact with gray rocks

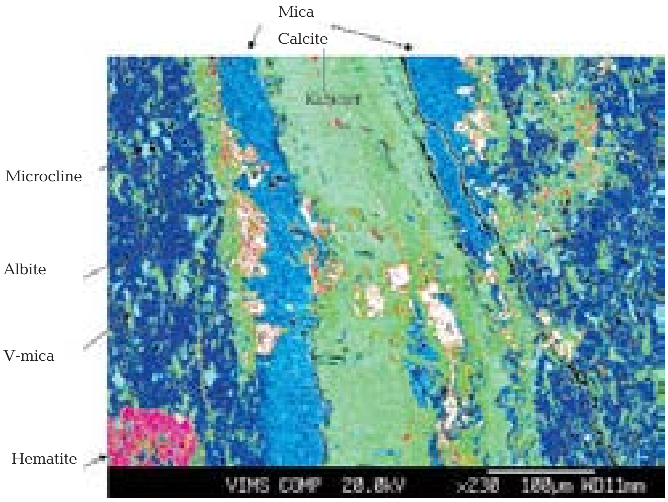
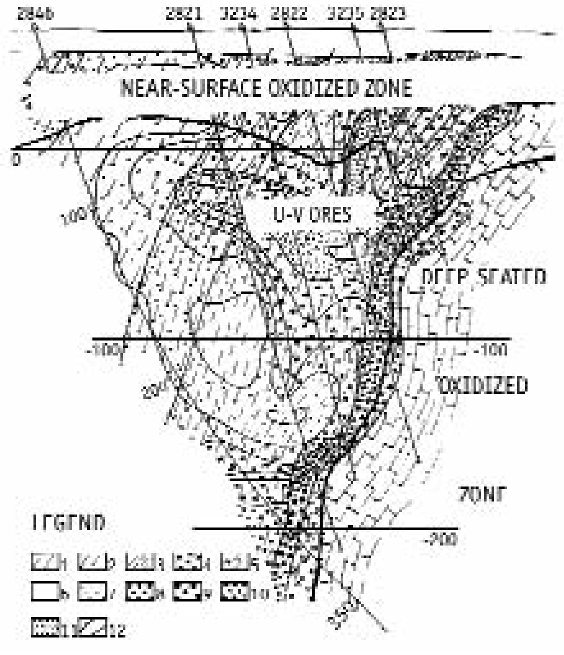


*Fig. 1. Albitized rocks with superimposed U-V mineralization and calcite, micaceous, and hematite veinlets and segregations and hydrated uranium oxides (light gray on the figure).*

*Fig. 2. Location of the near-surface and deep-seated oxidizing zones in regard to U-V ores at the Srednyaya Padma deposit. Geology after Poluekotov et al. (1998).*
*(1) Variegated clay-carbonate slate. (2) Greenish grey clay-carbonate slate. (3) Schungite-bearing clay slates with iterlayers of dolomite. (4) Feldspar-quartz siltstone and aleuroslate. (5) Dolomite. (6) Moraine. (7) First grade of metasomatic alteration. (8) Outer zone of metasomatic alteration. (9) Intermediate zone of metasomatic alteration. (10) Inner zone of metasomatic alteration. (11) Strongly brecciated ore. (12a) Boundaries of lithologic units. (12b) Boundaries of metasomatic zones.*



and hematite veinlets are enriched in redeposited minerals of noble metals and, locally, uranium and vanadium. Conventional mineralogical methods failed to identify these minerals. Therefore, the high-resolution techniques, including scanning electron microscopy with an energy-dispersion system (SEM-EDS), transmitted-electron microscopy (TEM) with X-ray microdiffraction, and electron-microprobe analysis were used to detect ultramicroscopic concentration centers of noble metals, their chemical composition, structure and morphology.

The noble metals in the Onega ores are irregularly distributed. The maximum contents occur in the roscoelite-chromceladonite-dolomite veinlets that cut the U-V ores. According to most researchers, these veinlets are hydrothermal. Padmaite, PdBiSe, sudovikovite, $PtSe_2$ (Polekhovskii *et al.*, 1991; 1997), and malyshevite, $PdBiCuS_3$ (Chernikov *et al.*, 2006), the new minerals of Pd and Pt were firstly described from such veinlets at the largest Srednyaya Padma deposit. In addition to roscoelite, chromceladonite and dolomite, clausthalite, PbSe, froodite, $PdBi_2$, and native gold and bismuth are abundant in the veinlet, whereas moncheite, $PtTe_2$, sobolevskite, PdBi, insizwaite, $Pt(Bi,Sb)_2$, bogdanovichite, $AgBiSe_2$, polarite, $Pd_2PbBi$, and paraguanajuatite, $Bi_2Se_2S$, are less abundant. As is apparent, noble metals occur as selinides, and less frequently, as selenide-sulfides, tellurides and bismuthides, or are constitutive compounds with bismuth, lead and other elements. For example, in addition to froodite, intermediate members compositionally close to urvantsevite $Pd(Bi,Pb)_2$ were identified (Table 1).

The noble metal minerals are associated with oxides (nasturane and hydrated nasturane) and uranium silicates of the coffinite type, vanadium micas, and selenides of lead, copper, and bismuth.

Carbonate segregations with redeposited fine-grained native copper, auricupride, native platinum, froodite,

*Table 1.* **Composition of froodite and intermediate member between froodite and urvantsevite**

| Component | Pd, wt% | Bi | Pb | Se | Pt | Total | Formula |
|---|---|---|---|---|---|---|---|
| 1 | 20.6 | 78.9 | 2.4 | 0.2 | – | 102.1 | $Pd(Bi,Pb)_2$ |
| 2 | 18.0 | 70.8 | 9.3 | 1.6 | – | 101.3 | $Pd(Bi,Pb)_2$ |
| 3 | 17.6 | 66.8 | 11.8 | 2.8 | 1.5 | 100.5 | $Pd(Bi,Pb)_2$ |
| 4 | 21.8 | 78.2 | – | 0.2 | – | 100.2 | $PdBi_2$ |

*Table 2.* **Content of noble metals in the studied samples**

| Depth | 87.7 m | 87.7 m | 153 m | 153 m | 166.5 m |
|---|---|---|---|---|---|
| | 1 an. | 2 an. | 1 an. | 2 an. | |
| Pt, ppm | 0.3 | 0.22 | 0.4 | 0.27 | 0.24 |
| Pd | 0.2 | 3.35 | 0.9 | 0.56 | 9.87 |
| Au | 9.3 | 0.28 | – | 0.25 | 0.2 |
| Ag | 0.2 | 0.2 | – | 1.0 | 0.49 |

isoferoplatinum, intermetallic CuZn, iron-group intermetallides, and a novel natural phase $Cu_3Pd$, the palladium analogue of auricupride (Chernikov *et al.*, 2005) are observed in the near-surface and deep-seated oxidized zones at Srednyaya Padma. The size of these grains ranges from 1 – 5 nm to 300 – 500 nm.

A grain with diffuse reflections of the phase AuO(OH) was observed in hematitized dolomites. This is the second natural finding; the first one was described from weathering crusts in the South Urals (Novgorodova *et al.*, 1995). All above mineral phases were found in samples with a total noble-metal content of 10 ppm and higher. However, in most of the near-surface and deep-seated oxidized zones, the total content of noble metals ranges from 0.n to ~10 ppm.

Modes of occurrence of noble metals in samples of the Tsarevskoe deposit collected from the near-surface oxidized zone at a depth of 87.7 m below the surface and from dolomite in the deep-seated zone at depths of 153 and 166.5 m below the surface were described for the first time by Dubinchuk *et al.* (2007). Conventional mineralogical techniques showed that the dolomite is highly silicified, limonized, and impregnated with Mn oxides. Dolomites from the deep-seated oxidized zone are hematized and silicified, and contain native copper, apatite and rare vanadium mica. Like previous data (Dubinchuk *et al.*, 2007), the content of noble metals determined by chemical and spectral methods ranges from 0.*n* to 9.87 ppm (Table 2). Segregations of noble metals have been not identified using SEM-EDS in the samples with such a content. Therefore, these samples were examined with TEM followed by extraction of phases and their identification by X-ray microdiffraction and electron-microprobe analysis.

Segregations of native gold were found in the near-surface oxidized zone at a depth of 87.7 m. They are square, irregular-shaped, and occasionally oval fine clusters (Fig. 3a). Extracted particles to replica are distinguished by both ring and discrete-point X-ray single-crystal microdiffraction patterns, which are characteristic of gold (Fig. 3b).

Numerous inclusions of apatite and sporadic grains of native copper and sphalerite were identified in quartz from dolomites collected at a depth of 153 m. With detection limits (wt.%) of 0.02 Ag, 0.06 Au, 0.06 Pd, and 0.01 Pt, the elevated contents of noble metals in the sample and in these minerals were not measured. Spindle-shaped particles of native gold, which are partly broken and leached, were found by TEM (Fig. 4a). Extracted particles are characterized by a ring X-ray microdiffraction pattern that is characteristic of metallic gold (Fig. 4b).

Different size (not less than n0.0 nm) segregations of native copper (including bladed ones), and individual crystals of gold disseminated in these blades (Fig. 5a) were observed in samples from the 166.5 m depth (closer to the middle part of the deep-seated oxidized zone). The blades are transparent to electrons and the gold crystals appear dark. Results of investigation of the bladed areas by TEM equipped with EDS are given in Table 3. Only in point 1 in native copper is Au below detection limit. However, more than 8% Ag and about 7% Co were identified in this point. At other points, more than 27% Au and 12% Ag are observed.

The polycrystalline texture of the transparent blade was established by X-ray microdiffraction (circles in Fig. 5a). In addition to the distinct reflections of native copper, weak reflections of native gold are present in the microdiffraction patterns (Fig. 5b). The gold crystals in native copper are oriented: $(111)_{Au}$ coincides with $(111)_{Cu}$. Fine grains of native platinum characterized by the clear

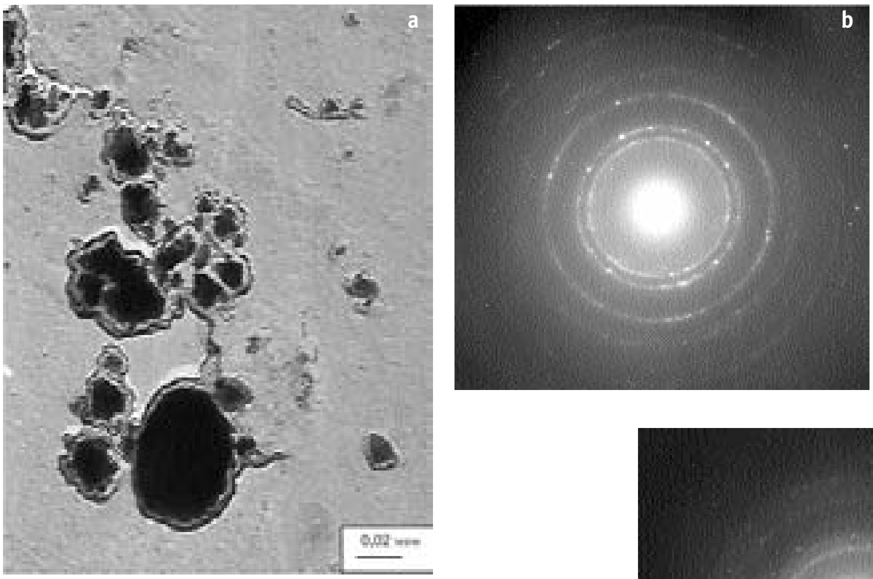


*Fig. 3. Features of native gold from the near-surface oxidizing zone.*

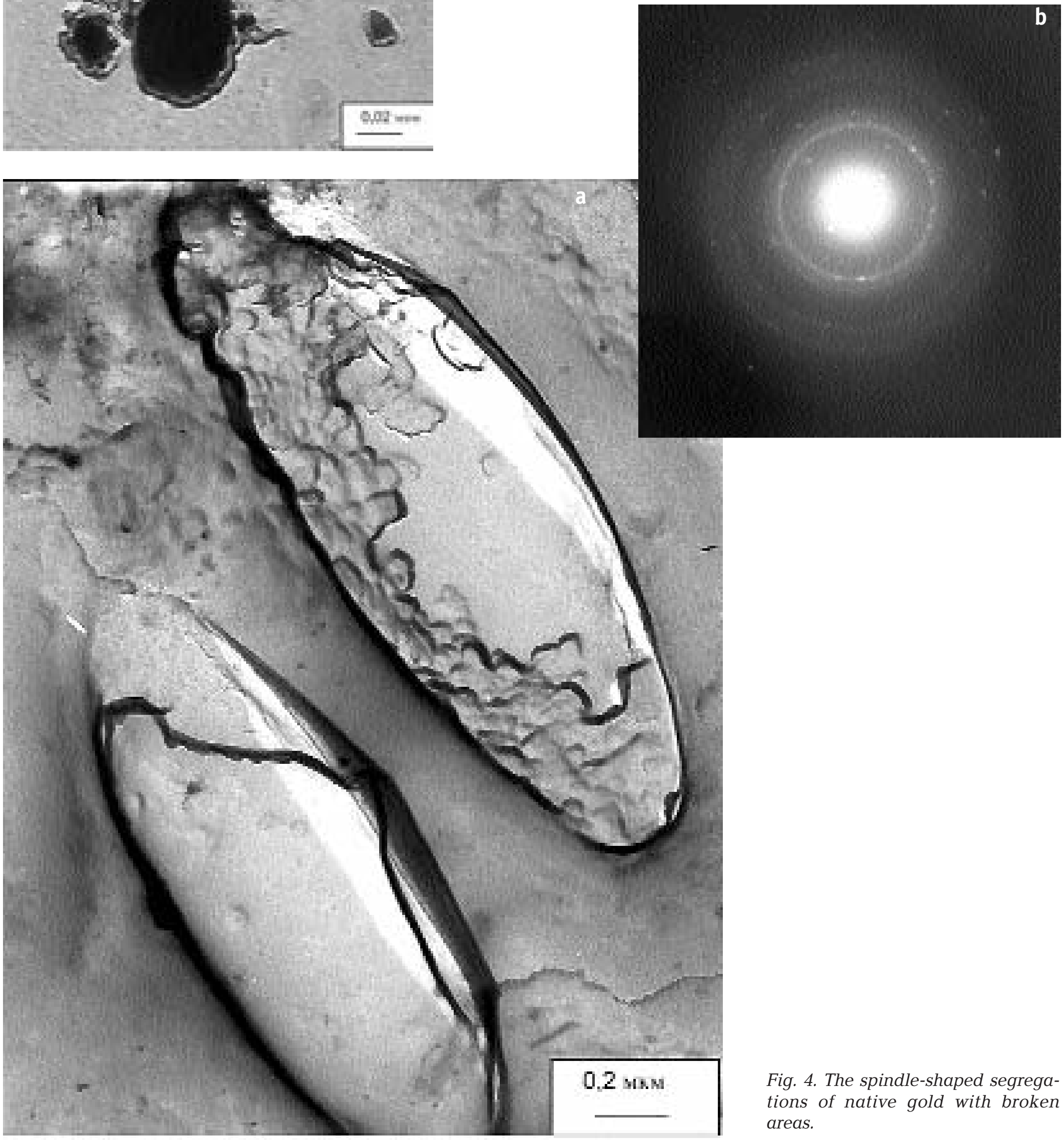


*Fig. 4. The spindle-shaped segregations of native gold with broken areas.*

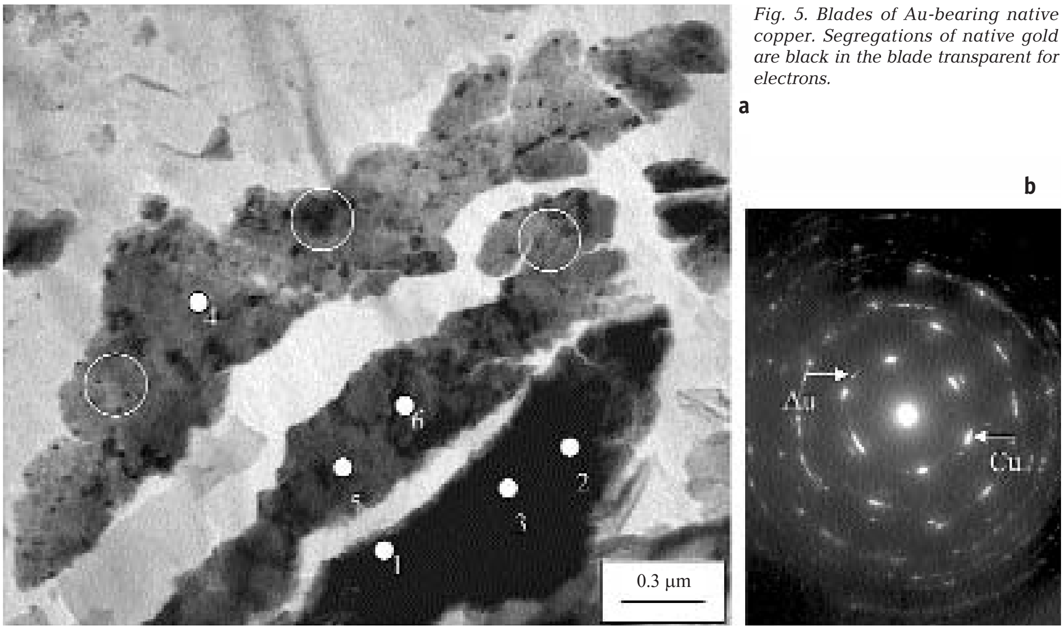


*Fig. 5. Blades of Au-bearing native copper. Segregations of native gold are black in the blade transparent for electrons.*

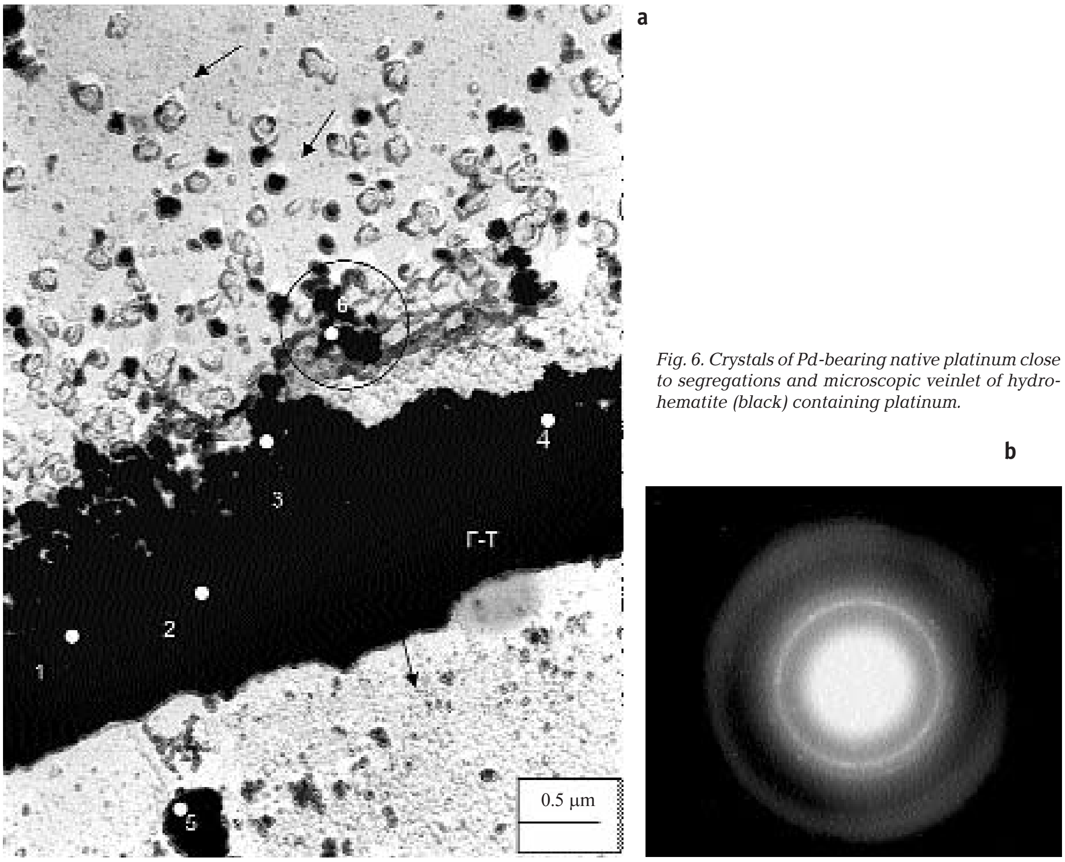


*Fig. 6. Crystals of Pd-bearing native platinum close to segregations and microscopic veinlet of hydrohematite (black) containing platinum.*

*Table 3.* **Composition of separate areas of native copper blade (wt%)**

| №№ | Ca | Ag | Ni | Co | Cu | Au | Total |
|---|---|---|---|---|---|---|---|
| 1 | 0.00 | 8.59 | 0.00 | 7.11 | 84.30 | 0.00 | 100.00 |
| 2 | 12.48 | 12.36 | 0.48 | 0.00 | 47.28 | 27.41 | 100.01 |
| 3 | 12.48 | 12.35 | 0.48 | 0.00 | 47.28 | 27.41 | 100.00 |
| 4 | 14.17 | 12.52 | 1.07 | 0.00 | 44.87 | 27.37 | 100.00 |
| 5 | 13.17 | 12.34 | 0.81 | 0.00 | 46.33 | 27.34 | 99.99 |
| 6 | 10.51 | 12.17 | 0.01 | 0.00 | 50.05 | 27.26 | 100.00 |

*Table 4.* **Composition of native platinum, wt %**

| №№ | Si | Ca | Fe | Co | Ni | Pt | Pd | Total |
|---|---|---|---|---|---|---|---|---|
| 1 | 2.89 | 0.11 | 13.72 | 1.19 | 1.22 | 46.58 | 30.21 | 95.92 |
| 2 | 1.75 | 0.14 | 10.17 | 1.44 | 1.84 | 54.45 | 24.17 | 93.96 |
| 3 | 1.11 | 1.45 | 6.18 | 1.55 | 1.97 | 60.74 | 22.81 | 95.81 |
| 4 | 1.27 | 2.00 | 1.75 | 1.58 | 0.00 | 58.41 | 16.00 | 81.01 |
| 5 | 0.22 | 2.15 | 1.26 | 1.21 | 2.17 | 65.48 | 27.70 | 100.19 |
| 6 | 0.97 | 2.29 | 0.54 | 1.51 | 1.98 | 65.62 | 27.01 | 99.92 |

X-ray microdiffraction pattern (Fig. 6b) were found, with particles located above the veinlets of hydrohematite (Fig. 6a) being larger (portions of μm) in comparison with those below the veinlet (0.0n μm). The points shown in Fig. 6a correspond to the analyses listed in Table 4.

Pt concentration ranges from ~ 46.6 to ~65.6%, Pd, from 16.0 to 30.2%, and Fe, from ~13.7 to 0.54%. Despite the absence of any positive linear correlation between platinum and iron, the largest PGE concentration is observed with the lowest Fe content (slightly higher than 0.5% at point 6).

As listed in Table 2, the noble metals are extremely unevenly distributed in the examined samples and Pd content is higher than Pt, but discrete phases of Pd were not identified. Nanocrystals of the Pd analogue of auricupride overgrown by hematite were previously described by Chernikov et al (2005). Such segregations of Pd are probable characteristic of the studied samples.

In general, modern high resolution techniques allow characterization of the mineralogical features of the hydrothermal veins and near-surface and deep-seated oxidized zones at these deposits. The noble metal minerals occur as selenides, selenide-sulfides and compounds with Bi, Te, and Pb in hydrothermal roscoelite-chromceladonite-dolomite veinlets. In contrast to these hydrothermal veinlets, grains of native copper, gold, and platinum with palladium, nanocrystals of auricupride, phase AuO(OH), the new natural Pd analogue of auricupride, and CuZn intermetallic compounds, which are usually observed with carbonate material, are prevalent in the near-surface and deep-seated oxidized zones. Gold grains from the near-surface oxidized zone (above the bedded deep-seated oxidized zone) with the low content of noble metals (less than 10 ppm), are square, anhedral, or oval fine clusters up to 0.1 μm in size. In the upper part of the deep-seated oxidized zone, gold occurs as broken spindle-shaped particles 2-3 μm in size. Closer to the middle part of the deep-seated oxidized zone, the gold crystals are disseminated in blades of native copper up to tens of μm in size; the blades are polycrystalline and the gold crystals are oriented parallel to the copper crystals. Segregations of Pd-bearing native platinum also occur here. Thus, the results obtained indicate that leaching and redistribution of noble metals decrease with depth in the oxidized zone with total content of these metals less than 10 ppm. At the same time, the size of gold grains increases downward, suggesting larger concentrations of noble metals at depth. Together with previous data (Chernikov *et al.*, 2005), this conclusion suggests significant increase of noble-metal reserves near explored U-V deposits.

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