*Mineralogical Magazine, June 2017, Vol. 81(3), pp. 531–541*

# Norilskite, $(Pd,Ag)_7Pb_4$, a new mineral from Noril'sk-Talnakh deposit, Russia

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[*Received 15 January 2016; Accepted 25 May 2016; Associate Editor: Sergey Krivovichev*]

**ABSTRACT**

Norilskite, $(Pd,Ag)_7Pb_4$ is a new platinum-group mineral discovered in the Mayak mine of the Talnakh deposit, Russia. It forms anhedral grains in aggregates (up to ~400 μm) with polarite, zvyagintsevite, Pd-rich tetra-auricupride, Pd-Pt bearing auricupride, Ag-Au alloys, (Pb,As,Sb) bearing atokite, mayakite, Bi-Pb-rich kotulskite and sperrylite in pentlandite, cubanite and talnakhite. Norilskite is brittle, has a metallic lustre and a grey streak. Values of $VHN_{20}$ fall between 296 and 342 kg mm$^{-2}$, with a mean value of 310 kg mm$^{-2}$, corresponding to a Mohs hardness of ~4. In plane-polarized light, norilskite is orange-brownish pink, has moderate to strong bireflectance, orange-pink to greyish-pink pleochroism, and strong anisotropy; it exhibits no internal reflections. Reflectance values of norilskite in air ($R_o$, $R_e$, in %) are: 51.1, 48.8 at 470 nm, 56.8, 52.2 at 546 nm, 59.9, 53.5 at 589 nm and 64.7, 55.5 at 650 nm. Sixteen electron-microprobe analyses of natural norilskite gave an average composition: Pd 44.33, Ag 2.68, Bi 0.33 and Pb 52.34, total 99.68 wt.%, corresponding to the empirical formula $(Pd_{6.56}Ag_{0.39})_{\sum 6.95}(Pb_{3.97}Bi_{0.03})_{\sum 4.00}$ based on 4 Pb + Bi atoms; the average of eight analyses on synthetic norilskite is: Pd 42.95, Ag 3.87 and Pb 53.51, total 100.33 wt.%, corresponding to $(Pd_{6.25}Ag_{0.56})_{\sum 6.81}Pb_{4.00}$. The mineral is trigonal, space group $P3_121$, with $a = 8.9656(4)$, $c = 17.2801(8)$ Å, $V = 1202.92(9)$ Å$^3$ and $Z = 6$. The crystal structure was solved and refined from the powder X-ray diffraction data of synthetic $(Pd,Ag)_7Pb_4$. Norilskite crystallizes in the $Ni_{13}Ga_3Ge_6$ structure type, related to nickeline. The strongest lines in the powder X-ray diffraction pattern of synthetic norilskite [*d* in Å (*I*) (*hkl*) ] are: 3.2201(29)(023,203), 2.3130(91)(026,206), 2.2414(100)(220), 1.6098(28)(046,406), 1.3076(38)(246,462), 1.2942(18)(600), 1.2115(37)(22.12,12.13), 0.9626(44)(06.12,60.12). The mineral is named for the locality, the Noril'sk district in Russia.

**Keywords:** norilskite, platinum-group mineral, $(Pd,Ag)_7Pb_4$ phase, electron-microprobe data, reflectance data, X-ray diffraction data, crystal structure, Mayak mine, Talnakh deposit, Noril'sk district, Russia.

## Introduction

The holotype specimen (polished section), that contains norilskite, ideally $(Pd,Ag)_7Pb_4$, comes from the massive pentlandite-cubanite-talnakhite ore from the Mayak mine in the Talnakh deposit of the Noril'sk district, Russia. The sample was found at coordinates: 69°30′20″N and 88°27′17″E. The phase with the corresponding chemical composition, described as unnamed $(Pd,Ag)_2Pb$, has also been observed in the massive pentlandite-cubanite-talnakhite ore in the Komsomolsky mine of the Talnakh deposit and in the massive pentlandite-talnakhite ore in Zapolyarny (Trans-Polar) mine of the Noril'sk I deposit (Sluzhenikin and Mokhov, 2015). Norilskite formed in post magmatic conditions, with decreasing temperature (Sluzhenikin and Mokhov, 2015), most likely below 400°C.

The ore deposits of the Noril'sk-Talnakh district are associated with hypabyssal intrusions related to

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https://doi.org/10.1180/minmag.2016.080.125

the Siberian flood basalt province. Different types of ore can be distinguished in terms of sulfide content, metal proportions and position within the host intrusion. Extensive studies have been dedicated to Noril'sk ores and deposits (e.g. Genkin *et al.*, 1981; Genkin and Evstigneeva, 1986; Distler *et al.*, 1988; Naldrett *et al.*, 1992; Czamanske *et al.*, 1992; Komarova *et al.*, 2002; Sluzhenikin, 2011; Sluzhenikin and Mohkov, 2015; among others).

Almost half of all known named platinum-group minerals have been reported from the Noril'sk ores, and also a number of unidentified phases. Furthermore, 17 new platinum-group minerals, among other minerals, have been discovered from the Noril'sk deposits.

## Mineral name and type material

Both mineral and name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA No. 2015-008). The mineral is named for the locality, the Noril'sk district, Russia. The mineral name norilskite was proposed for an alloy of Pt-Pd-Fe-Ni-Cu found in places near the Noril'sk deposits by Zviagincev (1940). However, Genkin (1968) proved that it was a mixture of several PGE minerals. Since that time no mineral species with the name norilskite have been proposed.

The holotype (polished section) is deposited at the Department of Earth Sciences of the Natural History Museum, London, UK, catalogue No. BM 2015, 1 and co-type material (polished section) is deposited in the Fersman Mineralogical Museum, Moscow, Russia, catalogue No. 4694/1.

## Appearance, physical and optical properties

Norilskite forms anhedral grains (~10 to 20 μm in diameter, in the type material the grain reaches almost 400 μm) in aggregates with polarite, zvyagintsevite, Pd-rich tetra-auricupride, Pd-Pt bearing auricupride, Ag-Au alloys, (Pb,As,Sb) bearing atokite, mayakite, Bi-Pb rich kotulskite and sperrylite in pentlandite, cubanite and talnakhite. A sample of norilskite (No. 229) with associated minerals of the type material from the Mayak mine is shown in Fig. 1.

Norilskite is opaque with a metallic lustre and grey streak. The powder of synthetic norilskite is grey in colour. The mineral is brittle. Values of $VHN_{20}$ measured from nine indentations is in the range from 296 to 342 kg mm$^{-2}$, with a mean value of 310 kg mm$^{-2}$, which corresponds to a Mohs hardness of ~4. The density calculated on the basis of the empirical formula is 12.99 g cm$^{-3}$. In plane-polarized reflected light, norilskite is orange-brownish pink, has moderate to strong bireflectance, strong from orange-pink ($R_o$) to greyish orange-pink ($R_{e'}$) pleochroism, and strong anisotropy with rotation tints from dull yellow to dull blue in partially crossed polars. It exhibits no internal reflections.

Reflectance measurements were made in air relative to a WTiC standard on both natural and synthetic norilskite using a J & M TIDAS diode array spectrometer attached to a Zeiss Axiotron microscope. The results are tabulated (Table 1) and illustrated in Fig. 2. With $R_o > R_e$ norilskite is uniaxial (–).

## Chemical composition

Chemical analyses were performed with a CAMECA SX-100 electron microprobe analyser (EMPA) in wavelength-dispersive mode using an electron beam focused to 1–2 μm. Pure elements were used as standards. Concentrations were quantified on the Pd*L*α, Ag*L*α, Bi*M*α and Pb*M*α (with overlap correction on Ag*L*α and Bi*M*α) with an accelerating voltage of 15 keV, and a beam current of 10 nA on the Faraday cup. Other elements were below the detection limit.

The electron-microprobe results are given in Table 2. The analyses of three grains from the Mayak mine, Talnakh deposit gave close compositions with slightly variable Pd:Ag ratio (based on 4 Pb + Bi atoms): $(Pd_{6.56}Ag_{0.42})_{\sum 9.98}(Pb_{3.97}Bi_{0.03})_{\sum 4.00}$ (No. 229), $(Pd_{6.47}Ag_{0.38})_{\sum 6.85}(Pb_{3.98}Bi_{0.02})_{\sum 4.00}$ (No. 208), $(Pd_{6.66}Ag_{0.37})_{\sum 7.03}(Pb_{3.97}Bi_{0.03})_{\sum 4.00}$ (No. 136) with the empirical formulae for the average analysis ($n = 16$) $(Pd_{6.56}Ag_{0.39})_{\sum 6.95}(Pb_{3.97}Bi_{0.03})_{\sum 4.00}$. The proposed simplified formulae for norilskite is $(Pd,Ag)_7Pb_4$ with $Z = 6$. Table 2 also shows alternative recalculations of the empirical formulae of norilskite based on one Pb + Bi atom per formula unit ($Z = 24$) and on 11 atoms per formula unit ($Z = 6$). Nevertheless, in accordance with the crystal structure investigations (see 'Structure description' section) we favour $(Pd,Ag)_7Pb_4$ formulae based on 4 Pb + Bi atoms.

## Synthetic analogue

Tiny intergrowths of norilskite with lamellae of polarite and other minerals listed above embedded

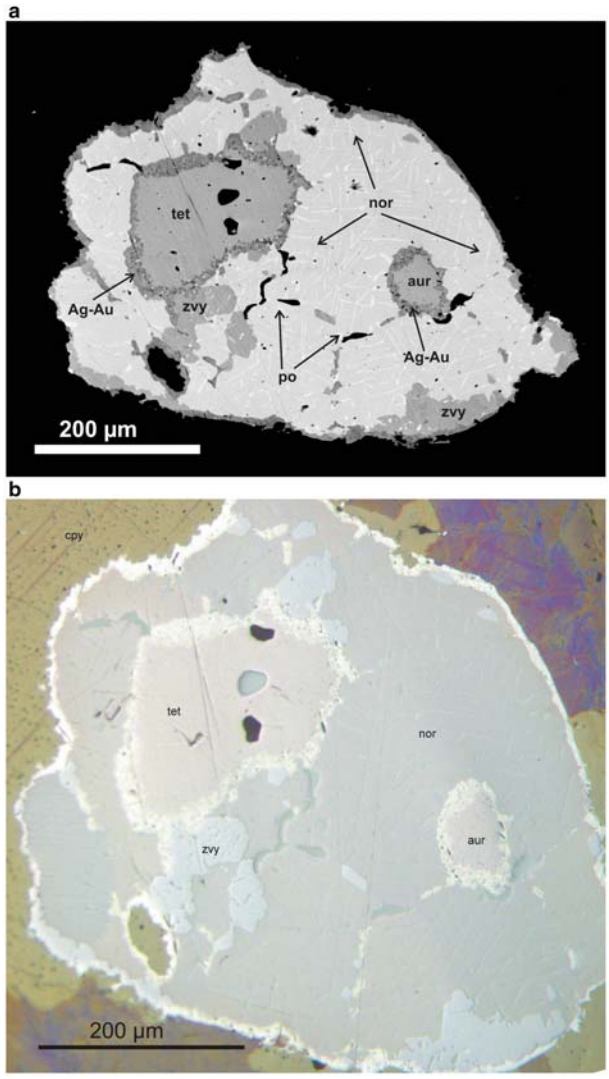


FIG. 1. Images of norilskite (nor) from the type locality Mayak mine of the Talnakh deposit, Noril'sk district (Sample No. 229) and associated minerals. (*a*) Back-scattered electron (BSE) image; (*b*) reflected light photomicrograph of the same grain, zvyagintsevite (zvy), auricupride (aur), tetra-auricupride (tet), polarite (po) and Ag-Au alloys.

in pentlandite prevented its extraction and isolation in an amount sufficient for the relevant crystallographic and structural investigations. Therefore these investigations were performed on the synthetic phase $(Pd_{6.25}Ag_{0.56})_{\sum 6.81}Pb_{4.00}$.

The synthetic phase $(Pd_{6.25}Ag_{0.56})_{\sum 6.81}Pb_{4.00}$ was prepared in an evacuated and sealed silica-glass tube in a horizontal furnace in the Laboratory of Experimental Mineralogy of the Czech Geological Survey in Prague. To prevent loss of material to the vapour phase during the experiment, the free space in the tube was reduced by placing a closely fitting glass rod against the charge. The temperature was measured with Pt-PtRh thermocouples and is accurate to within ±3°C. A charge of ~200 mg was carefully weighed out from the native elements. We used, as starting chemicals silver powder (Aldrich Chem. Co., 99.999% purity), lead ingot (Aldrich Chem. Co., 99.999% purity) and palladium powder (Aldrich Chem. Co., 99.95%

TABLE 1. Reflectance data for natural and synthetic norilskite.

| | natural | | synthetic | |
|---|---|---|---|---|
| λ (nm) | *Ro* (%) | *Re′* (%) | *Ro* (%) | *Re′* (%) |
| 400 | 46.6 | 44.9 | 47.1 | 45.1 |
| 420 | 47.9 | 45.9 | 48.4 | 46.1 |
| 440 | 49.0 | 46.9 | 49.6 | 47.3 |
| 460 | 50.4 | 48.2 | 51.1 | 48.7 |
| **470** | **51.1** | **48.8** | **51.8** | **49.4** |
| 480 | 51.8 | 49.4 | 52.5 | 50.0 |
| 500 | 53.3 | 50.4 | 53.9 | 51.2 |
| 520 | 54.7 | 51.2 | 55.3 | 52.2 |
| 540 | 56.3 | 52.0 | 56.7 | 53.2 |
| **546** | **56.8** | **52.2** | **57.1** | **53.5** |
| 560 | 57.9 | 52.5 | 58.1 | 54.1 |
| 580 | 59.7 | 53.1 | 59.6 | 54.9 |
| **589** | **59.9** | **53.5** | **59.9** | **55.2** |
| 600 | 61.1 | 53.8 | 61.2 | 55.6 |
| 620 | 62.7 | 54.4 | 62.3 | 56.5 |
| 640 | 64.0 | 55.1 | 63.9 | 57.2 |
| **650** | **64.7** | **55.5** | **64.4** | **57.7** |
| 660 | 65.4 | 55.8 | 65.0 | 58.1 |
| 680 | 66.6 | 57.0 | 66.4 | 59.0 |
| 700 | 67.8 | 58.1 | 67.5 | 60.0 |

Note: The values required by the Commission on Ore Mineralogy are given in bold.

purity). The starting mixture was first melted at 1000°C for two days. The product was then (from melting at 1000°C) ground in an agate mortar under acetone and reheated to 300°C for 113 days. The sample was quenched by dropping the capsule in cold water.

## X-ray crystallography

A few grains of synthetic material were tested using single-crystal diffraction, however all the crystals examined were found unsuitable for single-crystal analysis. Therefore, the crystal structure and unit-cell parameters of synthetic norilskite were refined from the powder X-ray diffraction (XRD) data.

The powder XRD pattern used for the Rietveld refinement and refinement of lattice parameters was collected in Bragg-Brentano geometry on an X´Pert Pro PANalytical diffractometer, equipped with X´Celerator detector and a Co*K*α radiation source. The data were collected in the 15–135°2θ range. The details of data collection and basic crystallographic data are given in Table 3.

Inspection of the powder diffraction pattern of the synthetic analogue of norilskite indicated a positive match with the PDF-2 card no. 42-798 (ICDD, 2002) denoted as the $Pd_6AgPb_4$ phase and the $Pd_3Pb$ phase as a minor admixture (PDF-2 card no. 50-1631). The existence of a synthetic phase

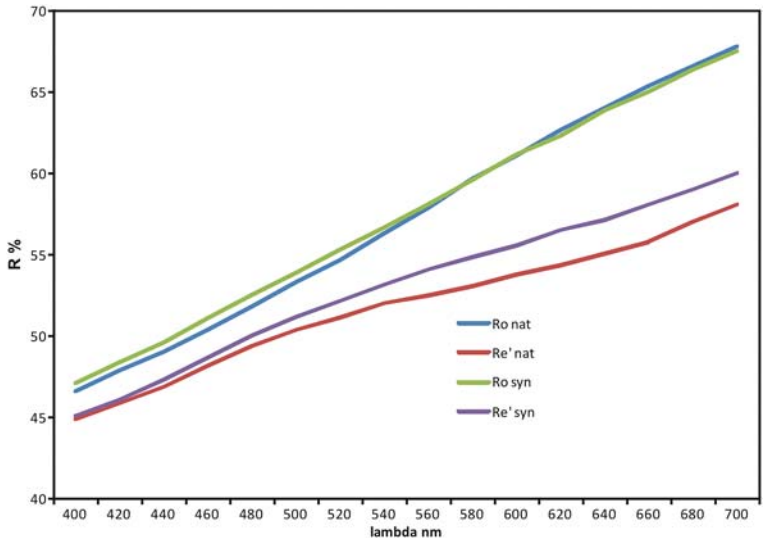


FIG. 2. Reflectance data for natural norilskite compared to synthetic norilskite in air. The reflectance values (*R*%) are plotted *vs*. wavelength λ in nm.

TABLE 2. Electron-microprobe analyses of natural and synthetic norilskite and three recalculations of norilskite stoichiometry (based on Pb + Bi = 4 atoms per formula unit (apfu), Pb + Bi = 1 apfu and 11 apfu).

| | Natural sample | | | | | $(Pd,Ag)_7Pb_4$ (Z = 6) | | | $(Pd,Ag)_{2-x}Pb$ (Z = 24) | | | $(Pd,Ag)_7Pb_4$ (Z = 6) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | wt.% | | | | | Pb = 4 | | | Pb = 1 | | | apfu 11 | | | |
| No. | Pd | Ag | Pb | Bi | Total | Pd | Ag | Pb + Bi | Pd | Ag | Pb + Bi | Pd | Ag | Pb | Bi |
| 229 (2) | 45.01 | 2.91 | 52.30 | 0.44 | 100.66 | 6.65 | 0.42 | 4.00 | 1.66 | 0.11 | 1.00 | 6.60 | 0.42 | 3.94 | 0.03 |
| | 44.39 | 3.20 | 52.42 | 0.32 | 100.34 | 6.56 | 0.47 | 4.00 | 1.64 | 0.12 | 1.00 | 6.54 | 0.46 | 3.97 | 0.02 |
| | 44.65 | 2.78 | 52.71 | 0.39 | 100.53 | 6.55 | 0.40 | 4.00 | 1.64 | 0.10 | 1.00 | 6.58 | 0.40 | 3.99 | 0.03 |
| | 44.02 | 2.84 | 52.35 | 0.43 | 99.63 | 6.50 | 0.41 | 4.00 | 1.62 | 0.10 | 1.00 | 6.55 | 0.42 | 4.00 | 0.03 |
| | 44.80 | 2.85 | 53.07 | 0.36 | 101.07 | 6.53 | 0.41 | 4.00 | 1.63 | 0.10 | 1.00 | 6.57 | 0.41 | 3.99 | 0.03 |
| avg ($n$ = 5) | *44.57* | *2.91* | *52.57* | *0.39* | *100.44* | *6.56* | *0.42* | *4.00* | *1.64* | *0.11* | *1.00* | *6.57* | *0.42* | *3.98* | *0.03* |
| 208 | 44.84 | 2.88 | 52.94 | 0.25 | 100.91 | 6.57 | 0.42 | 4.00 | 1.64 | 0.10 | 1.00 | 6.58 | 0.42 | 3.99 | 0.02 |
| | 43.56 | 2.60 | 52.62 | 0.19 | 98.97 | 6.43 | 0.38 | 4.00 | 1.61 | 0.09 | 1.00 | 6.54 | 0.39 | 4.06 | 0.01 |
| | 44.21 | 2.52 | 52.47 | 0.34 | 99.54 | 6.52 | 0.37 | 4.00 | 1.63 | 0.09 | 1.00 | 6.59 | 0.37 | 4.02 | 0.03 |
| | 44.35 | 2.52 | 53.09 | 0.35 | 100.31 | 6.46 | 0.36 | 4.00 | 1.62 | 0.09 | 1.00 | 6.57 | 0.37 | 4.04 | 0.03 |
| | 43.64 | 2.76 | 53.14 | 0.25 | 99.80 | 6.37 | 0.40 | 4.00 | 1.59 | 0.10 | 1.00 | 6.51 | 0.41 | 4.07 | 0.02 |
| | 44.59 | 2.48 | 53.21 | 0.29 | 100.57 | 6.49 | 0.36 | 4.00 | 1.62 | 0.09 | 1.00 | 6.58 | 0.36 | 4.03 | 0.02 |
| avg ($n$ = 6) | *44.20* | *2.63* | *52.91* | *0.28* | *100.02* | *6.47* | *0.38* | *4.00* | *1.62* | *0.09* | *1.00* | *6.56* | *0.38* | *4.03* | *0.02* |
| 136-2 | 44.25 | 2.31 | 51.23 | 0.12 | 97.91 | 6.71 | 0.35 | 4.00 | 1.68 | 0.09 | 1.00 | 6.68 | 0.34 | 3.97 | 0.01 |
| | 44.04 | 2.39 | 50.53 | 0.45 | 97.41 | 6.73 | 0.36 | 4.00 | 1.68 | 0.09 | 1.00 | 6.68 | 0.36 | 3.93 | 0.04 |
| | 44.09 | 2.46 | 52.06 | 0.31 | 98.92 | 6.56 | 0.36 | 4.00 | 1.64 | 0.09 | 1.00 | 6.61 | 0.36 | 4.01 | 0.02 |
| | 44.73 | 2.61 | 51.68 | 0.49 | 99.51 | 6.68 | 0.38 | 4.00 | 1.67 | 0.10 | 1.00 | 6.64 | 0.38 | 3.94 | 0.04 |
| | 44.12 | 2.82 | 51.57 | 0.35 | 98.86 | 6.62 | 0.42 | 4.00 | 1.65 | 0.10 | 1.00 | 6.60 | 0.42 | 3.96 | 0.03 |
| avg ($n$ = 5) | *44.24* | *2.52* | *51.41* | *0.35* | *98.52* | *6.66* | *0.37* | *4.00* | *1.66* | *0.09* | *1.00* | *6.64* | *0.37* | *3.96* | *0.03* |
| avg ($n$ = 16) | *44.33* | *2.68* | *52.34* | *0.33* | *99.68* | *6.56* | *0.39* | *4.00* | *1.64* | *0.10* | *1.00* | *6.59* | *0.39* | *3.99* | *0.03* |
| Std. dev. | 0.39 | 0.22 | 0.72 | 0.09 | | | | | | | | | | | |

| No. | Synthetic sample wt.% Pd | Ag | Pb | Total | $(Pd,Ag)_7Pb_4$ ($Z = 6$) Pb = 4 Pd | Ag | Pb | $(Pd,Ag)_{2-x}Pb$ ($Z = 24$) Pb = 1 Pd | Ag | Pb | $(Pd,Ag)_7Pb_4$ ($Z = 6$) apfu 11 Pd | Ag | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exp33 | 43.28 | 3.64 | 53.94 | 100.85 | 6.25 | 0.52 | 4.00 | 1.56 | 0.13 | 1.00 | 6.38 | 0.53 | 4.09 |
| | 42.63 | 4.34 | 53.07 | 100.03 | 6.26 | 0.63 | 4.00 | 1.56 | 0.16 | 1.00 | 6.32 | 0.63 | 4.04 |
| | 42.21 | 4.18 | 53.48 | 99.87 | 6.15 | 0.60 | 4.00 | 1.54 | 0.15 | 1.00 | 6.29 | 0.61 | 4.09 |
| | 43.19 | 3.63 | 53.67 | 100.50 | 6.27 | 0.52 | 4.00 | 1.57 | 0.13 | 1.00 | 6.39 | 0.53 | 4.08 |
| | 42.88 | 4.66 | 53.09 | 100.63 | 6.29 | 0.67 | 4.00 | 1.57 | 0.17 | 1.00 | 6.31 | 0.68 | 4.01 |
| | 42.80 | 3.43 | 53.25 | 99.48 | 6.26 | 0.49 | 4.00 | 1.57 | 0.12 | 1.00 | 6.40 | 0.51 | 4.09 |
| | 42.88 | 3.92 | 53.71 | 100.50 | 6.22 | 0.56 | 4.00 | 1.55 | 0.14 | 1.00 | 6.35 | 0.57 | 4.08 |
| | 43.72 | 3.19 | 53.89 | 100.79 | 6.32 | 0.45 | 4.00 | 1.58 | 0.11 | 1.00 | 6.45 | 0.46 | 4.08 |
| avg ($n = 8$) | *42.95* | *3.87* | *53.51* | *100.33* | *6.25* | *0.56* | *4.00* | *1.56* | *0.14* | *1.00* | *6.36* | *0.57* | *4.07* |
| Std. dev. | 0.42 | 0.46 | 0.32 | 0.45 | | | | | | | | | |

TABLE 3. Powder X-ray diffraction experimental details and Rietveld analysis of norilskite.

| | |
|---|---|
| **Crystal data** | |
| Space group | $P3_121$ |
| Unit-cell content | $Z = 6$ |
| Unit-cell parameters (Å) | $a = 8.9656(4)$<br>$c = 17.2801(8)$ |
| Unit-cell volume (Å$^3$) | 1202.92(9) |
| **Data collection** | |
| Radiation type, source | X-ray, Co$K\alpha$ |
| Generator settings | 40 kV, 30 mA |
| Range in 2θ (°) | 15–135 |
| Step size (°) | 0.02 |
| **Rietveld analysis** | |
| No. of reflections | 531 |
| No. of structural parameters | 31 |
| No. of. profile parameters | 4 |
| $R_{Bragg}$ | 0.098 |
| $R_p$ | 0.034 |
| $R_{wp}$ | 0.045 |
| Weighting scheme | $1/y_o$ |

$Pd_6AgPb_4$ is mentioned in the work of Sarah *et al.* (1981), where it is referred to as having the $Ni_{13}Ga_3Ge_6$ structure type. However, neither crystal coordinates nor chemical data for the $Pd_6AgPb_4$ phase have been published. The card no. 605653 for the $Pd_6AgPb_4$ phase, which can be found in the Inorganic Crystal Structure Database (2015), contains the same structural data (i.e. atomic coordinates) as has the card no. 52177 for the $Ni_{13}Ga_3Ge_6$ phase. Moreover, in the card 605653 is also a remark, that the coordinates were estimated by the database editor by the analogy to isotypic compounds. Therefore, the starting structure model of synthetic norilskite for subsequent Rietveld refinement was derived from the published data for the $Ni_{13}Ga_3Ge_6$ phase (Nover and Schubert, 1981). In this structure model, the Ni atoms (eight independent positions) were substituted by the Pd atoms, the Ge atoms (three independent positions) by the Pb atoms and the Ga atoms (two independent positions) by the Ag atoms. This initial structure model of synthetic norilskite (Pd39 Ag9 Pb18 atoms in the unit cell) was refined by the Rietveld method for the powder XRD data by means of the *FullProf* program (Rodríguez-Carvajal, 2006). The background was determined by the linear interpolation between consecutive breakpoints in the pattern. The refined parameters include those describing the peak shape

TABLE 4. Atomic positions for synthetic norilskite (space group $P3_121$, $B_{iso(overall)} = 0.12(2)$ Å$^2$), M(1)–M(7) represent Pd or/and Ag atoms.

| Atom | Wyckoff letter | *x* | *y* | *z* |
|---|---|---|---|---|
| M(1) | 3*a* | 0.492(5) | 0 | 1/3 |
| M(2) | 3*b* | 0.996(6) | 0 | 5/6 |
| M(3) | 6*c* | 0.998(7) | 0.503(5) | 0.3213(9) |
| M(4) | 6*c* | 0.507(5) | 0.006(5) | 0.162(1) |
| M(5) | 6*c* | 0.315(4) | 0.658(3) | 0.0930(9) |
| M(6) | 6*c* | 0.333(4) | 0.178(4) | 0.420(1) |
| M(7) | 6*c* | 0.153(3) | 0.343(4) | 0.259(1) |
| M(8) | 3*a* | 0.012(4) | 0 | 1/3 |
| M(9) | 3*b* | 0.497(7) | 0 | 5/6 |
| Pb(1) | 6*c* | 0.184(4) | 0.309(4) | 0.0839(6) |
| Pb(2) | 6*c* | 0.623(2) | 0.305(2) | 0.0852(7) |
| Pb(3) | 6*c* | 0.340(2) | 0.169(2) | 0.2545(5) |
| Pb(4) | 6*c* | 0.123(1) | 0.316(3) | 0.4129(7) |

and width, peak asymmetry, unit-cell parameters, fractional coordinates, occupancy parameters and an overall isotropic displacement parameter.

The occupancy parameters were tested carefully during the refinement (Pb against Pd, Ag against Pb), taking into account that it is not possible to distinguish between Ag and Pd atoms from conventional powder XRD data (Co*K*α radiation). Consequently, the occupancy at the Ag(2) position (6*c*) was changed from Ag to Pb atoms, as was suggested by a significant drop of an $R_{Bragg}$ factor (from 0.144 to 0.121) and a more reasonable coordination sphere for the other Ag atoms (octahedral coordination by Pb atoms). This substitution influences the chemical composition of the structure model. Whereas the former model contains Pd39 Ag9 Pb18 atoms in the unit-cell, the new one has Pd39 Ag3 Pb24 atoms in the unit cell (as a result of Ag → Pb substitution on position 6*c*). After recalculation for $Z = 6$, the structure-derived formula is $(Pd_{6.50}Ag_{0.50})_{\Sigma 7.00}Pb_{4.00}$, which is in a very good agreement with the chemical composition obtained from EMPA of the synthetic phase $(Pd_{6.25}Ag_{0.56})_{\Sigma 6.81}Pb_{4.00}$.

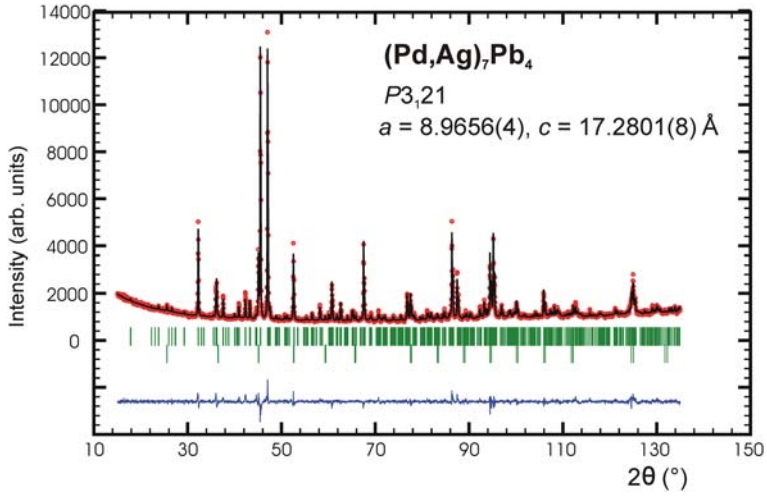


FIG. 3. Observed (circles), calculated (solid lines) and difference Rietveld profiles for norilskite. The upper reflection markers correspond to norilskite and the lower markers to a $Pd_3Pb$ (7 wt.%) impurity.

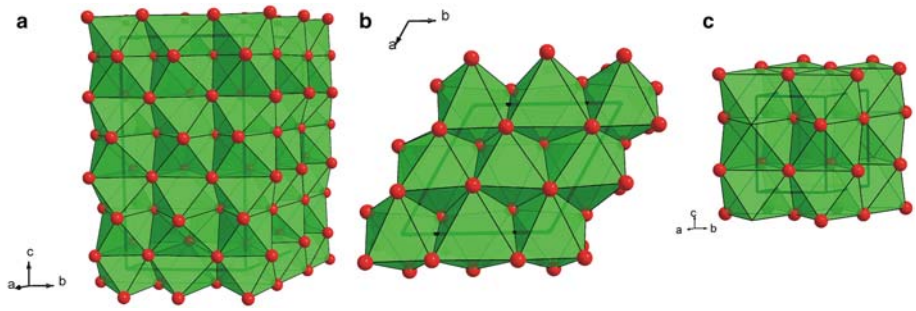


FIG. 4. Polyhedral representation of (*a*, *b*) the norilskite crystal structure showing the [$MPb_6$] distorted octahedra (M = Pd or Ag) and (*c*) the NiAs (nickeline) structure. Unit-cell edges are highlighted.

The final cycles of refinement converged to the residual factors: $R_{Bragg} = 0.098$, $R_{wp} = 0.045$ and $R_p = 0.034$. The crystal structure data are presented in Table 4, Fig. 3 shows the Rietveld plot. The crystal structure is depicted in Figs 4 and 5. As it is not possible to differentiate between Ag and Pd atoms in refinement from conventional powder XRD data, all non-Pb positions are denoted as M1-M9. The indexed powder-diffraction pattern of norilskite is given in Table 5.

## Structure description

The norilskite crystal structure can be viewed as a superstructure of the partially filled nickeline (NiAs) structure with doubled *a* and tripled *c* lattice parameters relative to the basic unit cell of the nickeline structure. In this basic structure, the As atoms form a hexagonal close packed (hcp) arrangement and Ni atoms occupy the octahedral interstices. This structure also contains trigonal-bipyramidal voids. If all of these voids are occupied, one arrives at the $Ni_2In$ structure type. In the norilskite crystal structure, the Pb atoms show distorted hexagonal close packing and all octahedral voids are occupied by M atoms (more specifically by M1, M2, M3, M4, M8 and M9 positions). The stoichiometry of such a hypothetical compound is MPb and its crystal structure has the NiAs structure topology. However, 75% of available trigonal-bipyramidal voids are occupied by additional M atoms (M5, M6, M7 positions) in the norilskite crystal structure. This partial occupation results in a ratio of (Pd + Ag)/Pb = 1.75 which corresponds very well with the ratio 1.70 obtained from the EMPA of synthetic material.

The partial occupation of trigonal-bypiramidal voids in norilskite implies short interatomic distances between M and Pb atoms, by comparison with the Pd–Pb distances observed in zvyagintsevite (2.85 Å; Ellner, 1981) and the $PdPb_2$ phase

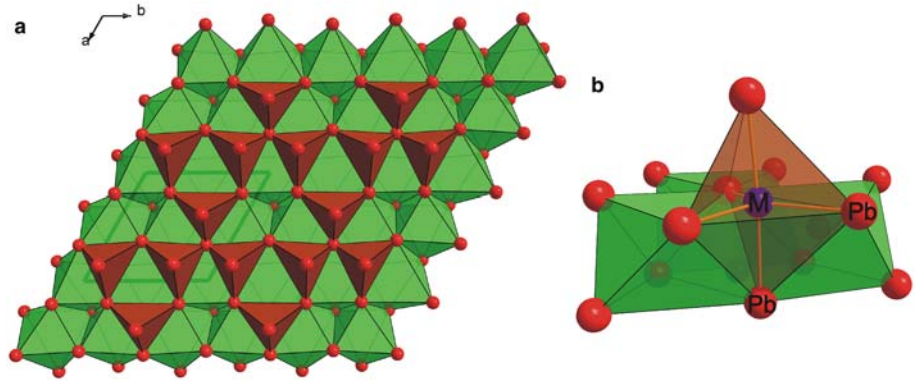


FIG. 5. (*a*) View along the *c* axis showing a layer composed of [$MPb_6$] edge-sharing octahedra (green) and trigonal-bipyramidal sites (brown) occupied by additional M atoms (M = Pd,Ag), (*b*) detailed view of the trigonal-bipyramidal site.

TABLE 5. Powder X-ray diffraction data for synthetic norilskite (Co*K*α radiation). Reflections with intensities ≥ 1% are shown.

| *h* | *k* | *i* | | $I_{(obs)}$ | $I_{(calc)}$ | $d_{(obs)}$ | $d_{(calc)}$ |
|---|---|---|---|---|---|---|---|
| 0 | 2 | 3 | } | 29 | 13 | 3.2201 | 3.2192 |
| 2 | 0 | 3 | } | | 15 | | 3.2192 |
| 1 | 2 | 1 | | 8 | 7 | 2.8905 | 2.8932 |
| 0 | 0 | 6 | | 11 | 13 | 2.8819 | 2.8801 |
| 1 | 2 | 2 | | 7 | 6 | 2.7788 | 2.7787 |
| 0 | 3 | 1 | | 4 | 4 | 2.5584 | 2.5595 |
| 0 | 3 | 2 | } | 8 | 2 | 2.4790 | 2.4792 |
| 3 | 0 | 2 | } | | 5 | | 2.4792 |
| 1 | 2 | 4 | } | 6 | 1 | 2.4274 | 2.4275 |
| 2 | 1 | 4 | } | | 6 | | 2.4275 |
| 0 | 2 | 6 | } | 91 | 59 | 2.3130 | 2.3131 |
| 2 | 0 | 6 | } | | 40 | | 2.3131 |
| 2 | 2 | 0 | | 100 | 100 | 2.2414 | 2.2413 |
| 1 | 2 | 7 | | 2 | 3 | 1.8886 | 1.8891 |
| 0 | 4 | 3 | } | 6 | 3 | 1.8396 | 1.8394 |
| 4 | 0 | 3 | } | | 2 | | 1.8394 |
| 2 | 2 | 6 | | 13 | 15 | 1.7690 | 1.7688 |
| 0 | 2 | 9 | } | 6 | 4 | 1.7212 | 1.7211 |
| 2 | 0 | 9 | } | | 4 | | 1.7211 |
| 1 | 4 | 2 | } | 4 | 2 | 1.6626 | 1.6626 |
| 4 | 1 | 2 | } | | 2 | | 1.6626 |
| 0 | 4 | 6 | } | 28 | 12 | 1.6098 | 1.6096 |
| 4 | 0 | 6 | } | | 19 | | 1.6096 |
| 5 | 0 | 1 | | 3 | 3 | 1.5467 | 1.5466 |
| 0 | 0 | 12 | | 11 | 11 | 1.4402 | 1.4401 |
| 1 | 5 | 2 | } | 3 | 2 | 1.3767 | 1.3767 |
| 5 | 1 | 2 | } | | 2 | | 1.3767 |
| 5 | 1 | 4 | | 2 | 2 | 1.3271 | 1.3271 |
| 2 | 4 | 6 | } | 38 | 23 | 1.3076 | 1.3074 |
| 4 | 6 | 2 | } | | 15 | | 1.3074 |
| 6 | 0 | 0 | | 18 | 18 | 1.2942 | 1.2941 |
| 2 | 5 | 2 | | 3 | 3 | 1.2307 | 1.2306 |
| 2 | 2 | 12 | } | 37 | 36 | 1.2115 | 1.2115 |
| 1 | 2 | 13 | } | | 3 | | 1.2108 |
| 2 | 5 | 4 | } | 4 | 3 | 1.1950 | 1.1948 |
| 5 | 2 | 4 | } | | 2 | | 1.1948 |
| 4 | 4 | 0 | | 11 | 11 | 1.1208 | 1.1207 |
| 5 | 2 | 8 | | 4 | 3 | 1.0776 | 1.0776 |
| 2 | 6 | 6 | } | 15 | 5 | 1.0086 | 1.0085 |
| 6 | 2 | 6 | } | | 9 | | 1.0085 |
| 0 | 6 | 12 | } | 44 | 20 | 0.9626 | 0.9625 |
| 6 | 0 | 12 | } | | 20 | | 0.9625 |

(2.95 Å; Havinga, 1972). The shortest interatomic contacts observed in the norilskite structure are 2.66 Å and 2.69 Å for M(7)–Pb(5) and M(5)–Pb(5) bonds, respectively. However, similar short metal–metal contacts were reported for the fully occupied $Ni_2In$ compound (Bhattacharya and Masson, 1976), so there seems to be no way to avoid such short interatomic distances in these compounds. On the other hand, partial occupancy of the trigonal bipyramidal voids might be a way to help the structure to relax (Norén *et al.*, 2000). The presence of vacancies seems to be an important stabilizing factor for the crystal structure of norilskite.

The alternative formulae of norilskite $(Pd, Ag)_{1.70}Pb_{1.00}$ based on one Pb atom per formula unit ($Z = 24$) clearly indicates its structural

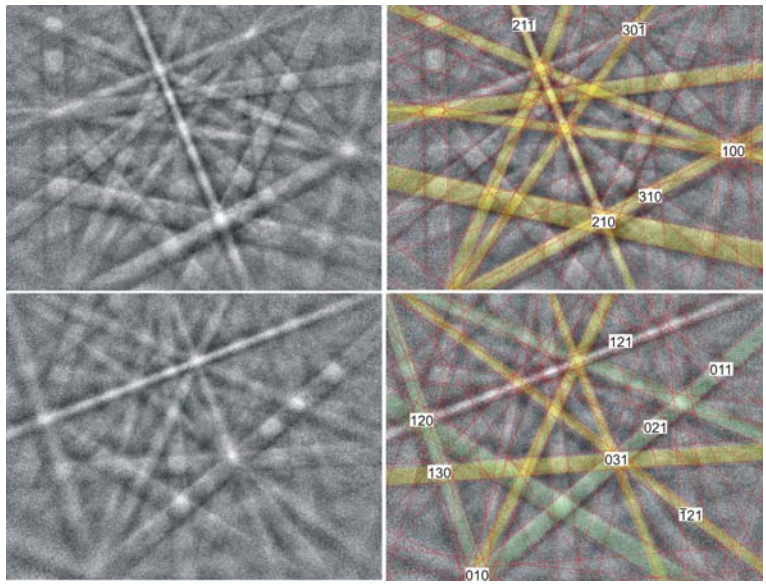


FIG. 6. EBSD image of natural norilskite; in the *right* pane, the Kikuchi bands are indexed.

relationship with the NiAs and $Ni_2In$ structures. It also shows a proportion of trigonal-bipyramidal voids, which are occupied by Ag and Pd atoms (i.e. 75% of available voids). However, we have decided for $(Pd,Ag)_7Pb_4$ ideal formulae ($Z = 6$), which reflects the fact that norilskite is an ordered superstructure relative to the NiAs and $Ni_2In$ structures. The presentation with $Pd_6(Pd,Ag)Pb_{4.00}$ formulae can also be considered as another alternative. Nevertheless, as we were not able to reveal a distinct Ag site from conventional XRD data, we prefer the $(Pd,Ag)_7Pb_4$ ideal formulae for norilskite. The EMPA data of the natural samples are also supportive for the $(Pd,Ag)_7Pb_4$ ideal formulae (Table 2).

## Proof of identity of natural and synthetic norilskite

The structural identity between the synthetic $(Pd,Ag)_7Pb_4$ and the natural material was confirmed by electron back-scattering diffraction (EBSD). For that purpose, we used a TESCAN Mira 3GMU scanning electron microscope combined with an EBSD system (NordlysNano detector, Oxford Instruments). The natural sample was prepared for investigation by re-polishing the surface with colloidal silica (OP-U) for 5 min to reduce the surface damage. The EBSD patterns were collected and processed using a proprietary computer program *AZtec HKL* (Oxford Instruments). The solid angles calculated from the patterns were compared with a synthetic $(Pd,Ag)_7Pb_4$ match containing 100 reflectors to index the patterns. The Kikuchi patterns obtained from the natural material (seven measurements on different spots on natural norilskite) were found to match the patterns generated from the structure of synthetic $(Pd,Ag)_7Pb_4$ provided by our crystal-structure determination (Fig. 6). The values of the mean angular deviation (MAD goodness-of-fit in the solution) between the calculated and measured Kikuchi bands range between 0.58° and 0.39°. These values reveal a very good match; mean angular deviations <1° are considered as indicators of an acceptable fit.

The EBSD study, chemical identity and optical properties confirmed the correspondence between natural and synthetic materials and thereby legitimize the use of the synthetic phase for the complete characterization of norilskite.

## Acknowledgements

The authors acknowledge Ulf Hålenius, Chairman of the CNMNC and its members for helpful comments on the submitted data. They also acknowledge the helpful comments of Louis J. Cabri and an

anonymous reviewer. The authors are grateful to Patricie Halodová and Jakub Haloda for carrying out the EBSD measurements. This work was supported by the internal project No. 331400 from the Czech Geological Survey.

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