

# Mertieite-II, Pd<sub>8</sub>Sb<sub>2.5</sub>As<sub>0.5</sub>, crystal-structure refinement and formula revision

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## ABSTRACT

The crystal structure of the mineral mertieite-II from the Kaarreoja River, Inari commune, Finnish Lapland, Finland, was refined to  $R_1 = 0.0222$  (I) and  $0.0228$  (II) on the basis of X-ray diffraction data collected from two single crystals. The mineral is trigonal, space group is  $R\bar{3}c$ . The unit-cell parameters for the two crystals are determined as:  $a = 7.5172(3)$ ,  $c = 43.037(2)$  Å,  $V = 2106.1(2)$  Å<sup>3</sup> (I);  $a = 7.5135(4)$ ,  $c = 43.003(3)$  Å,  $V = 2102.4(3)$  Å<sup>3</sup> (II) with  $Z = 12$ . The occupancies of the Sb and As position in the structure were refined according to the Sb:As ratio of each crystal. The position As1 (Wyckoff 6b) is completely filled by As atoms. Any excess of As is distributed together with Sb on structural position M1 (Wyckoff 12c). The crystal chemical formulae are defined as Pd<sub>8</sub>Sb<sub>1.5</sub>(Sb<sub>0.94</sub>As<sub>0.06</sub>)As<sub>0.5</sub> (crystal I) and Pd<sub>8</sub>Sb<sub>1.5</sub>(Sb<sub>0.88</sub>As<sub>0.12</sub>)As<sub>0.5</sub> (crystal II). As → Sb substitution of up to 4.50 wt% of As does not affect the main structural topology of mertieite-II. Mertieite-II, Pd<sub>8</sub>Sb<sub>2.5</sub>As<sub>0.5</sub> and synthetic Pd<sub>8</sub>Sb<sub>3</sub> are isotypic compounds. The crystal structures of synthetic Pd<sub>8</sub>Sb<sub>3</sub> and natural mertieite-II, Pd<sub>8</sub>Sb<sub>2.5</sub>As<sub>0.5</sub>, can be derived from the hexagonal close packing by filling additional layers between the close-packed 3<sup>6</sup> layers. The structure consists of Sb and (Sb,As) triangular 3<sup>6</sup>, Pd triangular 3<sup>6</sup> and Pd pentagonal-triangular 5.3<sup>3</sup> layers. Stacking of Sb-, (Sb,As)- and Pd-nets along the z axis caused extension of the unit cell. It contains a total of 36 layers: six Sb1-nets, six (M1, As1)-nets, 12 Pd1-nets and 12 (Pd1,Pd3,Pd4)-nets.

**KEYWORDS:** mertieite-II, crystal structure, single-crystal X-ray diffraction, 4-layers package, stacking layers.

## Introduction

THE mineral mertieite, with general formula Pd<sub>5+x</sub>(Sb,As)<sub>2-x</sub> was discovered in the Au-Pt concentrates at Goodnews Bay, Alaska (Desborough *et al.*, 1973). Those authors derived two types of composition for mertieite grains: mertieite-I, (Pd<sub>5.04</sub>Cu<sub>0.4</sub>)(Sb<sub>0.92</sub>As<sub>0.9</sub>) and mertieite-II, (Pd<sub>5.13</sub>Cu<sub>0.02</sub>)(Sb<sub>1.53</sub>As<sub>0.33</sub>).

After a few years the mertieite minerals were re-examined (Cabri *et al.*, 1975) and it was established that the composition of mertieite-II corresponds to Pd<sub>8</sub>(Sb,As)<sub>3</sub>, and the parameters of its rhombohedral unit cell are:  $a = 7.55$  Å,  $c = 43.18$  Å. Later Cabri (1980) gave the structural formula for the mineral as Pd<sub>16</sub>Sb<sub>5</sub>As ( $Z = 6$ ) with space group  $R\bar{3}c$  based on an unpublished crystal-structure determination. Arsenic atoms were located in a special position (As1), and the Sb to As ratio was found to be equal to 5:1.

McDonald and Cabri (2005) refined the crystal structure of mertieite-II up to  $wR_2 = 7.68\%$ . The structural formula was proposed as Pd<sub>48</sub>Sb<sub>15</sub>As<sub>3</sub>.

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The important role of single-crystal X-ray diffraction (XRD) in the study of mertieite-group minerals was emphasized.

The crystal structure of the synthetic antimony analogue of mertieite-II,  $\text{Pd}_8\text{Sb}_3$ , was determined by Wopernow and Schubert (1976) using single-crystal XRD. The structural model proposed was a non-centrosymmetric space group  $R\bar{3}c$ ,  $a = 7.6152$ ,  $c = 43.032$  Å,  $V = 2161.1$  Å<sup>3</sup>,  $Z = 12$ ; the reliability factor  $R$  of the solution was 14%. Marsh (1994) refined the structure using experimental data collected by Woperson to centrosymmetric space group  $RR\bar{3}c$ ; refinement gave  $R = 12.6\%$ .

The current study is devoted to the crystal-structure analysis of natural mertieite-II,  $\text{Pd}_8(\text{Sb}, \text{As})_3$ . The structure was refined successfully and the space group, coordinates of atoms in anisotropic form, site populations, interatomic distances and structural formula were defined.

## Material for investigation

The mertieite-II crystals for this structural refinement were received from Dr. Kari Kojonen, Geological Survey of Finland. They were collected from the black sands of gold placers from the Kaarrejoja River, Inari commune, Finnish Lapland, Finland (68,65°N, 25,63°E). The most probable source of the platinum-group minerals (PGM) is the mafic-ultramafic layered intrusions represented by gabbros and pyroxenites previously mapped as amphibolites that lie upstream of the sample-collection point (Meriläinen, 1976; Kojonen, 2011).

The PGMs from the black sands in the placer deposit are: sperrylite, isoferroplatinum, native platinum, Pt-oxide, braggite, cooperite, vysotskite, isomertieite, mertieite-I, mertieite-II, Os-Ir-Ru alloys, native Os, rustenburgite, palladseite and miessite (Kojonen *et al.* 2005, 2006, 2007, 2011; Kojonen, 2011). Further alloys of Pt-Cu, Pt-Pd, Au-Pd, Au-Sn, were reported. Undefined PGM phases are  $\text{PtPdAs}$ ,  $\text{PtPdAs}_2$ ,  $(\text{Pt,Cu,Fe})\text{Te}$ ,  $\text{Pd}_5\text{As}_2$  and  $\text{Pd}_{11}\text{Sb}_3\text{As}_2$ . Other heavy minerals discovered include thorianite, native Bi, cassiterite, columbite–tantallite, wolframite and monazite.

## Methods of study

Platinum-group mineral nuggets from the heavy fraction were mounted in an epoxy resin and a polished mount was prepared for examination by optical and scanning electron microscopy (SEM).

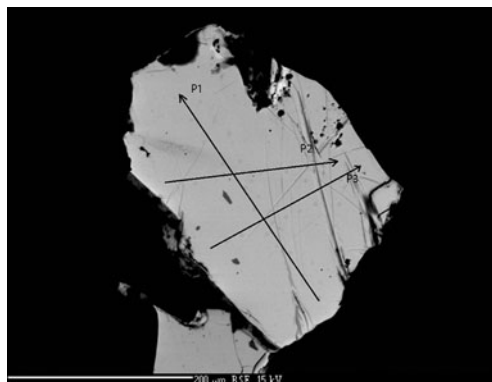


FIG. 1. Mertieite-II crystal I (SEM back-scattered electron image).

The chemical composition was determined using a Cameca SX 100 five spectrometer WDS instrument. The quantitative electron microprobe analyses (EMPA) were performed with an operating voltage of 15 kV, a beam current of 20 nA and a beam diameter of 1 μm. Pure Pd, Rh, Pt, cobaltite (for As),  $\text{Sb}_2\text{Te}_3$  (for Sb), chalcopyrite (for Cu and S) and hematite (for Fe) were used as reference materials.  $\text{AsL}\alpha$  (LIF diffracting crystal),  $\text{PdL}\alpha$  (LIF),  $\text{SbL}\alpha$  (PET),  $\text{SK}\alpha$  (PET),  $\text{FeK}\alpha$  (LIF),  $\text{RhL}\alpha$  (PET),  $\text{PtL}\alpha$  (LIF),  $\text{CuK}\alpha$  (LIF) spectral lines were used in the EPMA. The results obtained were used to select two grains of mertieite-II (Figs 1 and 2) for structural investigation (Table 1).

The grains were retrieved from the polished mount and analysed by single-crystal X-ray diffraction at the Center of X-ray diffraction studies at St. Petersburg State University (XRD

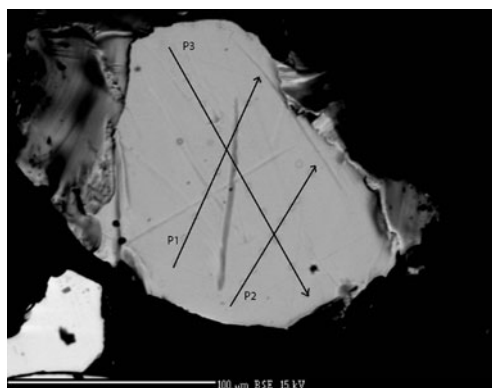


FIG. 2. Mertieite-II crystal II (SEM back-scattered electron image).

## MERTIEITE-II CRYSTAL-STRUCTURE REFINEMENT

TABLE 1. Representative\* compositions of mertieite-II (microprobe).

Element	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%
<b>Grain I</b>						
As	4.07 (3.80–4.31)	5.90	4.08 (3.96–4.31)	5.90	4.03 (3.94–4.17)	5.84
Pd	71.75 (71.13–72.40)	73.31	71.97 (71.40–72.40)	73.38	72.02 (71.34–72.60)	73.47
Sb	23.28 (23.06–23.47)	20.79	23.25 (23.09–23.39)	20.72	23.20 (23.09–23.30)	20.69
Sum	99.11		99.32		99.26	
Formula	**Pd <sub>8.06</sub> Sb <sub>2.29</sub> As <sub>0.65</sub> ***Pd <sub>8</sub> Sb <sub>2.27</sub> As <sub>0.64</sub>		**Pd <sub>8.07</sub> Sb <sub>2.28</sub> As <sub>0.65</sub> ***Pd <sub>8</sub> Sb <sub>2.26</sub> As <sub>0.64</sub>		**Pd <sub>8.08</sub> Sb <sub>2.28</sub> As <sub>0.64</sub> ***Pd <sub>8</sub> Sb <sub>2.28</sub> As <sub>0.64</sub>	
<b>Grain II</b>						
As	4.51 (4.25–4.65)	6.52	4.50 (4.37–4.63)	6.52	4.48 (4.27–4.87)	6.50
Pd	72.15 (71.64–72.63)	73.49	72.03 (71.36–72.48)	73.51	71.91 (71.36–71.44)	73.49
Sb	22.46 (22.39–22.55)	20.00	22.38 (22.15–22.49)	19.96	22.40 (22.14–22.70)	20.01
Sum	99.12		98.91		98.79	
Formula	**Pd <sub>8.09</sub> Sb <sub>2.20</sub> As <sub>0.72</sub> ***Pd <sub>8</sub> Sb <sub>2.18</sub> As <sub>0.71</sub>		**Pd <sub>8.09</sub> Sb <sub>2.20</sub> As <sub>0.72</sub> ***Pd <sub>8</sub> Sb <sub>2.17</sub> As <sub>0.71</sub>		**Pd <sub>8.08</sub> Sb <sub>2.20</sub> As <sub>0.72</sub> ***Pd <sub>8</sub> Sb <sub>2.18</sub> As <sub>0.71</sub>	

\*Average analysis along the profiles.

\*\*Calculated with 11 atoms per formula unit.

\*\*\*Calculated with 8 atoms of Pd per formula unit.

TABLE 2. Crystal data and structure refinement for mertieite-II.

Identification code	I	II
<b>Crystal data</b>		
Structural formula	Pd <sub>8</sub> Sb <sub>1.5</sub> (Sb <sub>0.94</sub> As <sub>0.06</sub> )As <sub>0.5</sub>	Pd <sub>8</sub> Sb <sub>1.5</sub> (Sb <sub>0.88</sub> As <sub>0.12</sub> )As <sub>0.5</sub>
Crystal system	trigonal	trigonal
Space group	<i>R</i> 3 <i>c</i>	<i>R</i> 3 <i>c</i>
<i>a</i> (Å)	7.5172(3)	7.5135(4)
<i>c</i> (Å)	43.037(2)	43.003(3)
<i>V</i> (Å <sup>3</sup> )	2106.1(2)	2102.4(3)
<i>Z</i>	12	12
<i>D</i> <sub>calc</sub> g/cm <sup>3</sup>	11.287	11.307
μ/mm <sup>-1</sup>	31.645	31.701
<b>Data collection</b>		
Diffractometer	Xcalibur Eos	Xcalibur Eos
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Temperature (K)	293(2)	293(2)
2θ range for data collection (°)	6 to 60	6 to 58
<i>R</i> <sub>int</sub> , <i>R</i> <sub>sigma</sub> (%)	2.84, 2.17	3.82, 2.12
<b>Refinement</b>		
Reflections collected	3548	5387
Independent reflections	656	608
Observed reflections [ <i>I</i> > 4σ ( <i>I</i> )]	574	567
Data/restraints/parameters	656/0/38	608/0/38
<i>S</i> (Goodness-of-fit on <i>F</i> <sup>2</sup> )	1.165	1.277
<i>R</i> [ <i>I</i> > 4σ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0222, <i>wR</i> <sub>2</sub> = 0.0448	<i>R</i> <sub>1</sub> = 0.0228, <i>wR</i> <sub>2</sub> = 0.0412
<i>R</i> [all data]	<i>R</i> <sub>1</sub> = 0.0291, <i>wR</i> <sub>2</sub> = 0.0466	<i>R</i> <sub>1</sub> = 0.0257, <i>wR</i> <sub>2</sub> = 0.0421
δρ (max)/(min) (e/Å <sup>-3</sup> )	1.28/−1.26	2.04/−1.16

TABLE 3. Atom coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for mertieite-II.

Atom	Site	x	y	z	ocf	U(eq)
<b>I</b>						
Pd1	36f	0.00068(8)	0.25365(8)	0.11468(1)	1	0.0079(2)
Pd2	36f	0.03583(8)	0.33597(8)	0.18415(1)	1	0.0072(2)
Pd3	12c	0	0	0.0589592	1	0.0071(2)
Pd4	12c	0	0	0.21848(2)	1	0.0069(2)
Sb1	18e	0.31913(8)	0	1/4	1	0.0059(2)
M1	12c	0	0	0.15803(2)	Sb = 0.94, As = 0.06	0.0070(2)
As1	6b	0	0	0	1	0.0059(3)
<b>II</b>						
Pd1	36f	0.00098(8)	0.25339(9)	0.11470(2)	1	0.0098(2)
Pd2	36f	0.03558(8)	0.33564(8)	0.18410(1)	1	0.0084(2)
Pd3	12c	0	0	0.05888(2)	1	0.0089(2)
Pd4	12c	0	0	0.21846(2)	1	0.0082(2)
Sb1	18e	0.31890(8)	0	1/4	1	0.0058(2)
M1	12c	0	0	0.15812(2)	Sb = 0.88, As = 0.12	0.0067(3)
As1	6b	0	0	0	1	0.0055(3)

Center SPbSU). Experimental data collection was achieved using an Agilent Technologies Xcalibur Eos diffractometer, which was operated at 50 kV and 40 mA. A hemisphere of three-dimensional data was collected at 293 K using monochromatic MoK $\alpha$  radiation. The data were integrated and corrected by means of the *CrysAlisPro* (Agilent Technologies, 2012) program package, which was also used to apply empirical absorption correction using spherical harmonics, implemented in the *SCALE3 ABSPACK* scaling algorithm. The

structures were solved by direct methods using the *SHELXT* program (Sheldrick, 2015). Four Pd positions, two Sb positions and one As site were located in the structure. The *SHELXL* program (Sheldrick, 2008) was used for the crystal-structure refinement. The population of the Sb and As sites was refined against Sb/As. The Sb1 and As1 site are occupied completely by Sb and As atoms, respectively. The site-occupancy factors of the M1 site were defined as Sb<sub>0.94</sub>As<sub>0.06</sub> (crystal I) and Sb<sub>0.88</sub>As<sub>0.12</sub> (crystal II). The structures were refined to R1 =

TABLE 4. Anisotropic displacement parameters ( $\text{\AA}^2$ ) for mertieite-II.

Atom	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
<b>I</b>						
Pd1	0.0054(3)	0.0086(3)	0.0082(3)	-0.0003(2)	-0.0002(2)	0.0024(2)
Pd2	0.0074(3)	0.0059(3)	0.0088(3)	0.0010(2)	0.0018(2)	0.0037(2)
Pd3	0.0068(3)	0.0068(3)	0.0077(4)	0	0	0.0034(1)
Pd4	0.0068(3)	0.0068(3)	0.0065(4)	0	0	0.0034(1)
Sb1	0.0052(2)	0.0053(3)	0.0073(3)	0.0009(2)	0.0005(1)	0.0027(2)
M1	0.0068(3)	0.0068(3)	0.0078(4)	0	0	0.0034(2)
As1	0.0050(5)	0.0050(5)	0.0077(7)	0	0	0.0025(2)
<b>II</b>						
Pd1	0.0052(3)	0.0130(3)	0.0077(3)	0.0006(2)	0.0010(2)	0.0020(2)
Pd2	0.0101(3)	0.0064(3)	0.0095(3)	0.0022(2)	0.0041(2)	0.0048(2)
Pd3	0.0093(3)	0.0093(3)	0.0081(4)	0	0	0.0046(2)
Pd4	0.0092(3)	0.0092(3)	0.0064(4)	0	0	0.0050(2)
Sb1	0.0051(3)	0.0059(3)	0.0052(3)	0.0021(2)	0.0010(1)	0.0030(2)
M1	0.0067(3)	0.0067(3)	0.0065(4)	0	0	0.0034(2)
As1	0.0051(5)	0.0051(5)	0.0065(8)	0	0	0.0025(2)

## MERTIETITE-II CRYSTAL-STRUCTURE REFINEMENT

TABLE 5. Interatomic distances (Å) for mertieite-II (crystal I) and (crystal II).

	I	II		I	II
Pd1–Sb1	2.6162(5)	2.6158(5)	Pd2–As1	2.4876(5)	2.4878(5)
M1	2.6657(7)	2.6641(8)	M1	2.6523(6)	2.6468(6)
Sb1	2.7230(7)	2.7210(7)	M1	2.7913(5)	2.7891(6)
Pd2	2.8521(7)	2.8496(7)	Pd2	2.8082(7)x2	2.8061(7)x2
Pd4	2.8579(6)	2.8599(6)	Pd2	2.8201(6)	2.8182(7)
Pd3	2.8668(6)	2.8657(6)	Sb1	2.8436(5)	2.8435(6)
Pd2	2.8793(7)	2.8776(8)	Pd1	2.8522(7)	2.8496(7)
Pd1	2.891(1)	2.891(1)	Pd1	2.8794(7)	2.8776(7)
Pd2	3.0378(7)	3.0323(2)	Pd3	2.9676(7)	2.9673(7)
Pd3	3.0624(8)	3.0615(1)	Pd1	3.0379(1)	3.0327(2)
Pd2	3.2119(7)	3.2143(1)	Pd2	3.2041(1)	3.1963(1)
Pd1	3.2979(1)x2	3.2912(1)x2	Pd1	3.2116(1)	3.2138(1)
Sb1	3.3402(1)	3.3407(1)	Pd4–Sb2	2.602(1)	2.595(1)
Pd3–As1	2.5372(8)	2.532(1)	Pd4	2.714(2)	2.712(2)
Sb1	2.7674(4)x3	2.7680(5)x3	Sb1	2.7561(7)x3	2.7534(7)x3
Pd1	2.8668(6)x3	2.8656(6)x3	Pd2	2.8201(7)x3	2.8182(7)x3
Pd2	2.9676(7)x3	2.9671(7)x3	Pd1	2.8579(6)x3	2.8599(6)x3
Pd1	3.0624(1)x3	3.0613(1) x3	M1–Pd4	2.602(1)	2.595(1)
Sb1–Pd1	2.6162(5)x2	2.6158(6)x2	Pd2	2.6523(6)x3	2.6468(6)x3
Pd1	2.7229(7)x2	2.7210(8)x2	Pd1	2.6657(7)x3	2.6641(8)x3
Pd4	2.7561(6)x2	2.7531(8)x2	Pd2	2.7913(5)x3	2.7891(6) x3
Pd3	2.7675(4)x2	2.7680(5)x2			
Pd2	2.8436(5)x2	2.8435(6)x2			
Pd1	3.3402(1)x2	3.3407(1)x2			
As1–Pd2	2.4876(5)x6	2.4878(5)x6			
Pd3	2.5372(8)x2	2.532(1)x2			

0.0222 for 574 (I) and  $R1 = 0.0228$  for 567 (II) unique observed reflections with  $|Fo| \geq 4\sigma F$ . The crystallographic data and selected refinement parameters are shown in Table 2. The final atomic

coordinates and displacement parameters are listed in Tables 3 and 4, and the selected interatomic distances are in Table 5. Table 6 shows the coordination numbers and the average values of the bond lengths.

 TABLE 6. The coordination numbers together with the average values of the Pd–Pd and Pd–Sb/As distances around the different atoms in mertieite-II and  $Pd_8Sb_3$ .

Central atom	CN(Pd)	$d_m$ (Å)		$Pd_8Sb_3$	CN(Sb/As)	$d_m$ (Å)		$Pd_8Sb_3$
		I	II			I	II	
Pd1	10	2.996	2.993	3.053	4	2.835	2.836	2.860
Pd2	9	2.943	2.946	2.986	4	2.692	2.694	2.717
Pd3	9	2.966	2.964	3.008	4	2.710	2.710	2.732
Pd4	7	2.821	2.821	2.815	4	2.718	2.714	2.746
Sb1	12	2.841	2.841	2.848				
M1	10	2.695	2.690	2.711				
As1*	8	2.500	2.499	2.613				

CN(Pd) is the number of nearest Pd neighbours; CN(Sb/As) the number of nearest Sb/As neighbours;  $d_m$  the average distance in Å.

\*Sb3 position on the  $Pd_8Sb_3$  structure.

TABLE 7. The compositions of mertieite-II from different localities.

Formula	Locality	References
$(\text{Pd}_{7.65}\text{Cu}_{0.34})_{\Sigma 7.99}(\text{Sb}_{2.71}\text{As}_{0.28}\text{Sn}_{0.02})_{\Sigma 3.01}$	Farm Tweefontein, Potgietersrust, Transvaal, South Africa	Cabri and Chen (1976)
$(\text{Pd}_{7.57}\text{Cu}_{0.42})_{\Sigma 7.99}(\text{Sb}_{2.67}\text{As}_{0.34})_{\Sigma 3.01}$	October deposit, Talnakh, Norilsk region, Russia	Kovalenker <i>et al.</i> (1978)
$(\text{Pd}_{7.93}\text{Ni}_{0.09})_{\Sigma 8.02}(\text{Sb}_{2.55}\text{As}_{0.35}\text{Te}_{0.08})_{\Sigma 2.98}$	Wellgreen deposit, Yukon, Canada	Barkov <i>et al.</i> (2002)
$\text{Pd}_{8.02}(\text{Sb}_{2.54}\text{As}_{0.39}\text{Bi}_{0.04})_{\Sigma 2.97}$	Sudbury, Ontario, Canada	Cabri and Laflamme (1976)
$\text{Pd}_{8.00}(\text{Sb}_{2.54}\text{As}_{0.46})_{\Sigma 3.00}$	Goodnews Bay, Alaska, USA, type locality	Cabri <i>et al.</i> (1975)
$\text{Pd}_{8.0}\text{Sb}_{2.5}\text{As}_{0.5}$	(ideal formula)	Cabri (2002)
$\text{Pd}_{8.12}(\text{Sb}_{2.46}\text{As}_{0.54})_{\Sigma 3.00}$	Goodnews Bay, Alaska, USA, type locality	Desborough <i>et al.</i> (1973)
$(\text{Pd}_{7.90}\text{Ni}_{0.05}\text{Fe}_{0.02}\text{Ir}_{0.01}\text{Pt}_{0.01}\text{Cu}_{0.01})_{\Sigma 8.00}$ $(\text{Sb}_{2.41}\text{As}_{0.57}\text{Pb}_{0.01}\text{S}_{0.01})_{\Sigma 3.00}$	Two Duck Lake, Northwestern Ontario, Canada	Watkinson and Ohnenstetter (1992)
$\text{Pd}_{8.07}\text{Sb}_{2.28}\text{As}_{0.65}$	Kaarreoja, Finnish Lapland, Finland	current study (crystal I)
$\text{Pd}_{8.08}\text{Sb}_{2.20}\text{As}_{0.72}$	Kaarreoja, Finnish Lapland, Finland	current study (crystal II)

### Chemical composition

The compositions of the two crystals were determined at ten points along each of three lines across each of the crystals (Figs 1 and 2). Table 1 presents the mean values for each profile. The compositions of the two crystals are nearly identical. In addition to Pd, As and Sb there are minor amounts of S (~0.04–0.05 wt.%) in some analyses. The As content in grain II is slightly higher than in the grain I. The Sb content is a little lower in grain II. The element concentrations vary within very narrow limits (~1 wt. %). The average element

contents (in wt.%) are: Pd 71.91, Sb 23.25, As 4.06 (grain I), and Pd 72.03, Sb 22.42, As 4.50 (grain II). They correspond to empirical formulae for crystals I and II, respectively, of:  $\text{Pd}_{8.07}\text{Sb}_{2.29}\text{As}_{0.65}$  (grain I) and  $\text{Pd}_{8.09}\text{Sb}_{2.20}\text{As}_{0.72}$  (grain II) calculated with 11 atoms per unit cell. The mertieite-II formulae calculated on the basis of 8 Pd atoms for samples I and II are  $\text{Pd}_8\text{Sb}_{2.27}\text{As}_{0.64}$  and  $\text{Pd}_8\text{Sb}_{2.18}\text{As}_{0.71}$ , respectively.

The calculated formulae are not completely identical with the general formula of mertieite-II (Table 7). Mertieite-II from the Kaarreoja River is characterized by a greater As content and a lower Sb

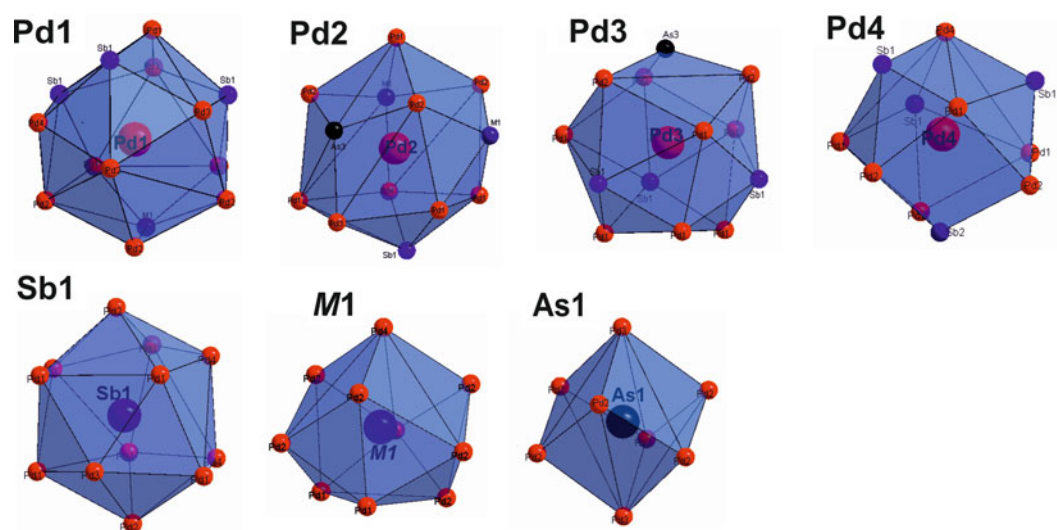


FIG. 3. Coordination polyhedrons of the mertieite-II structure.



content compared with mertieite-II from other localities.

## Crystal structure

The structure of mertieite-II contains four symmetrically independent Pd atom positions with two  $36f$  (Pd1 and Pd2) and two  $12c$  (Pd3 and Pd4) Wyckoff positions. The coordination polyhedra are: a Pd1-polyhedron that is a distorted Frank-Kasper polyhedron (14-vertex); the Pd2- and Pd3-polyhedra that are 13-vertex capped distorted icosahedra; and the Pd4 polyhedron that is an 11-vertex pentacapped trigonal prism (Fig. 3).

The Sb atoms occupy the positions:  $18e$  (Sb1, Coordination number (CN) = 12, icosahedra) and  $12c$  ( $M1$ , CN = 10, a four-capped trigonal prism). Arsenic atoms are located in the  $6b$  position (As1, CN = 8, square prism).

The unit cell of mertieite-II has a very elongated  $c$  parameter ( $\sim 43$  Å) (Fig. 4). Two types of triangular  $3^6$  nets of Sb and As atoms contribute to the structure (Fig. 5a,b). One type of net is built up only of Sb atoms in the Sb1 position; the other type of net consists of Sb and As atoms in both the  $M1$  and As1 positions. The ( $M1$ ,As1)-nets are slightly distorted with As and Sb atoms displaced above and below the (110) plane.

Palladium atoms are also located in net-like layers parallel to the (110) plane and there are two types of Pd-net. Palladium atoms in the Pd2 positions form a distorted triangular  $3^6$  net (Fig. 5c). Palladium atoms in the Pd1, Pd3 and Pd4 positions form a second Pd-net (Fig. 5d) which consists of pentagons and triangles which is known as a  $5.3^3$  net.

The Sb1- and ( $M1$ ,As1)-nets alternate along the  $z$  axis of the unit cell. Nets are also shifted relative to each other in the plane (110). The nets stack in such a way, that the unit cell of mertieite-II contains a total of 36 layers: six Sb1-nets, six ( $M1$ ,As1)-nets, 12 Pd1-nets and 12 (Pd1,Pd3,Pd4)-nets (Fig. 4). The stacking sequence is:  $A^1B^1C^1D^1C^2B^2A^2B^4C^3D^4C^4B^5A^3B^2C^5D^1C^6B^3A^1B^5C^7D^2C^8B^6A^2B^3C^9D^1C^{10}B^1A^3B^6C^{11}D^2C^{12}B^4$ , where the upper indexes denote layers in different orientations (Fig. 4).

The Sb-net and the (Sb,As)-net form a two-dimensional 'sandwich'-like package (Fig. 6). Palladium atoms occupy all of the octahedral and 5/6 of the tetrahedral interstices of the package. Thus there are two types of Pd-net inside the As,Sb-package the heights of which are  $\sim 1/3$  of

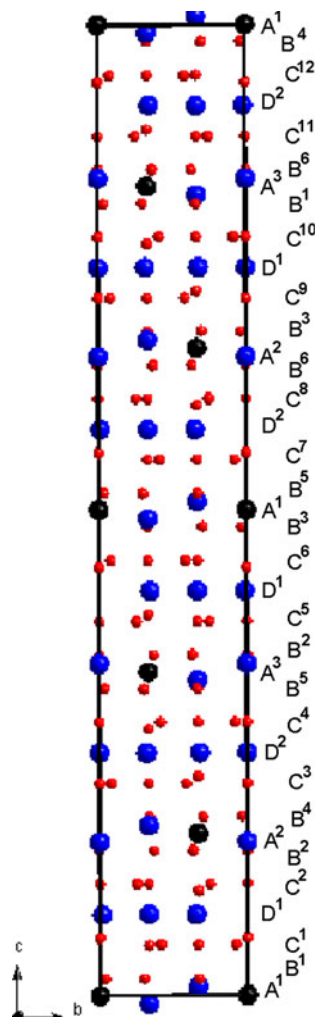


FIG. 4. Projection of the mertieite-II structure along the  $x$  axis. Sb atoms are drawn as large blue circles, As atoms as large black circles, Pd atoms as small red circles.

the interlayer distance above and below each As, Sb net (Fig. 6).

## Discussion

Mertieite-II is isostructural with the  $Pd_8Sb_3$  structure. The As  $\rightarrow$  Sb substitution of up to 4.50 wt.% in the mertieite-II was found not to affect the main structural topology. The unit-cell dimensions of synthetic  $Pd_8Sb_3$  are slightly higher ( $a = 7.6152$ ,  $c = 43.032$  Å,  $V = 2161.15$  Å<sup>3</sup>) than those of mertieite. The interatomic Pd-Pd distances do not

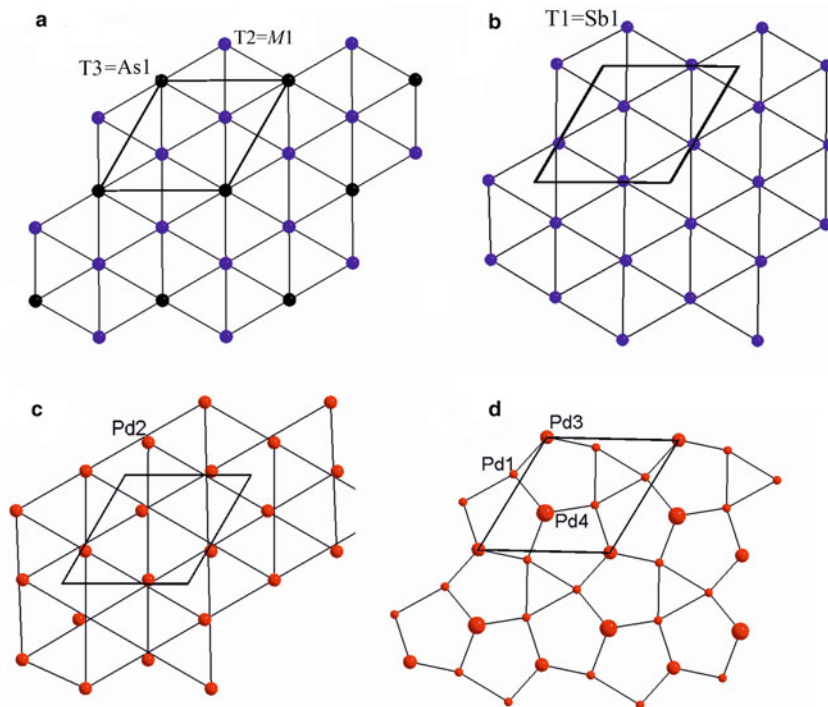


FIG. 5. Nets of atoms in the mertieite-II structure: (a) (Sb,As)-atoms  $3^6$  net, (b) Sb-atoms  $3^6$  net, (c) Pd-atoms  $3^6$  net, (d) Pd-atoms pentagon-triangular  $5.3^3$  net. The colour code is the same as in Fig. 4.

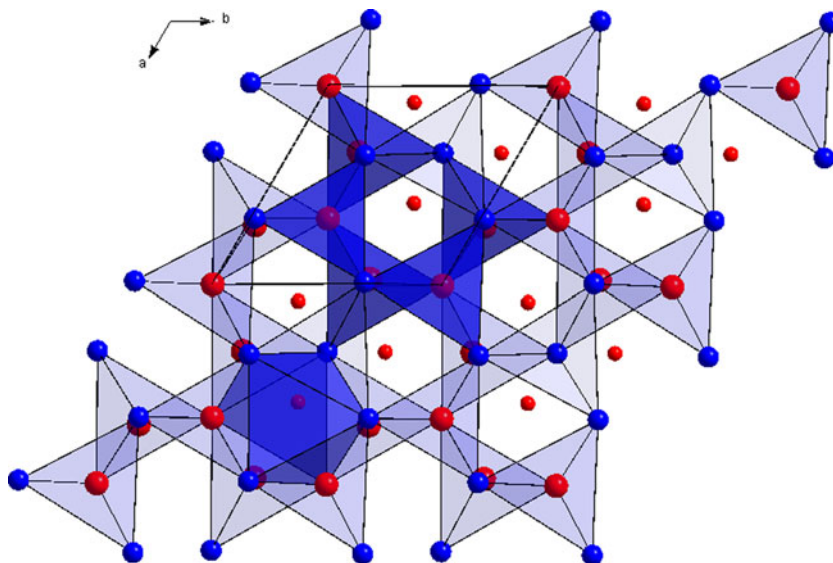


FIG. 6. A fragment of the mertieite-II structure: a two-dimensional 4-layer package is shown in the projection viewed down the  $z$  axis. The colour code is the same as in Fig. 4. Pd1 atoms (small red circles) occupy the octahedral voids (one octahedral void is shaded). Pd2, Pd3, Pd4 atoms (large red circles) occupy the tetrahedral voids (five tetrahedral voids are shaded).



## MERTIEITE-II CRYSTAL-STRUCTURE REFINEMENT

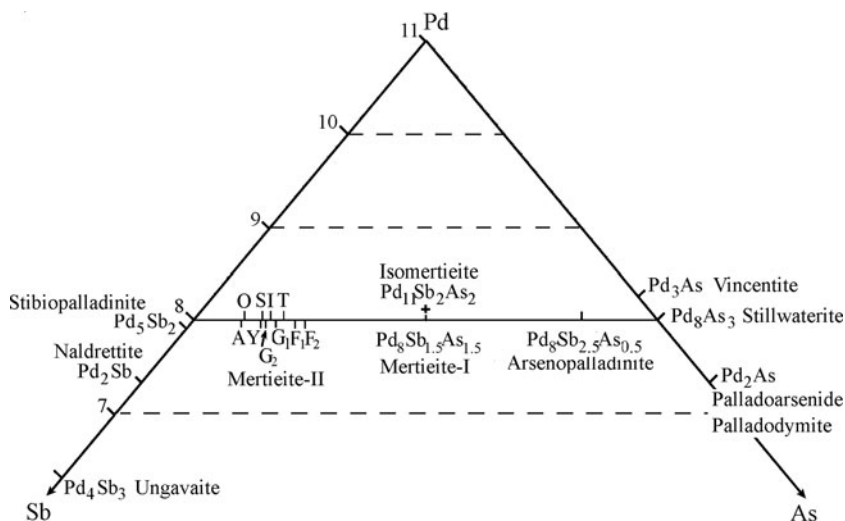


FIG. 7. Part of the Pd-Sb-As diagram: the range of mertieite-II compositions relate to other Pd-Sb-As minerals shown. Mertieite-II – the letters are the place names from Table 7: A = Africa, O = October, Y = Yukon, I = ideal formula, T = Two Duck Lake, S = Sudbury, G1 = Goodnews Bay (Desborough *et al.*, 1973), G2 = Goodnews Bay (Cabri *et al.*, 1975), F1 = Finland crystal 1, F2 = Finland crystal 2. Drawn to 11 atoms per formula unit. The small amounts of Sn, Bi, Te, Pb, S has been added to As.

differ significantly between these two structures (Table 6). The main difference between these two structures is the Pd–As and Pd–Sb atomic distances. The As1–Pd distances in the polyhedra around atoms at the 6b site are equal to 2.4878, 2.5322 Å (crystal I) and 2.4874, 2.5371 Å (crystal II) in the mertieite-II structure, in contrast to Sb3–Pd distances of 2.5944 and 2.668 Å, in the Pd<sub>8</sub>Sb<sub>3</sub> structure (Table 6). The volume of the polyhedra around the Sb2 atom site (12e position) also differ significantly. The Sb2–Pd bond lengths are larger in the mertieite-II structure (2.5948 to 2.7896 Å in crystal I and 2.602–2.7916 Å in crystal II) compared with 2.6594 to 2.7685 Å in the Pd<sub>8</sub>Sb<sub>3</sub> structure. The Sb1 polyhedron is highly distorted in natural mertieite-II: the Sb–Pd distances vary from 2.6158 to 3.3407 Å (crystal I), 2.6160–3.3402 Å (crystal II) whereas the Sb1 polyhedron is a little more regular in the Pd<sub>8</sub>Sb<sub>3</sub> structure and the range of the same distances is: 2.6561–3.3029 Å.

Pearson (1972) proposed a classification of metallic phases based on nets of atoms. The triangular As, Sb and Pd nets of the mertieite-II structure are the close-packed 3<sup>6</sup> layer according to Pearson's classification. The crystal structures of synthetic Pd<sub>8</sub>Sb<sub>3</sub> and natural mertieite-II, Pd<sub>8</sub>Sb<sub>2.5</sub>As<sub>0.5</sub>, can be derived from the hexagonal close packing by filling additional layers between the close-packed 3<sup>6</sup> layers.

Crystal-structure analysis of mertieite-II from the Kaarrejoja River placer confirmed that As atoms occupy a special position in the structure as indicated by previous studies of the mineral from other localities (Cabri, 1980; McDonald and Cabri, 2005). In the present investigation slightly more As-rich crystals were studied. The Sb- and As-site occupancies of the structure were analysed. The formulae of mertieite-II from the Kaarrejoja River defined by structural analysis are Pd<sub>8</sub>Sb<sub>1.5</sub>(Sb<sub>0.94</sub>As<sub>0.06</sub>)As<sub>0.5</sub> (crystal I) and Pd<sub>8</sub>Sb<sub>1.5</sub>(Sb<sub>0.88</sub>As<sub>0.12</sub>)As<sub>0.5</sub> (crystal II). These results are in relatively good agreement with formulae calculated from microprobe data: Pd<sub>8</sub>Sb<sub>2.27</sub>As<sub>0.64</sub> (crystal I) and Pd<sub>8</sub>Sb<sub>2.18</sub>As<sub>0.71</sub> (crystal II). Mertieite-II crystals from others localities have insufficient As content to completely fill the As1 site (Table 7 and Fig. 7). The Sb content of some of the mertieite-II grains is greater than the capacity of all of the Sb sites in the structure. Therefore, the excess Sb may also occupy the As1 site. The general formula of mertieite-II is Pd<sub>8</sub>(Sb,As)<sub>3</sub> (Cabri, 2002). Note, however, that Pd<sub>8</sub>As<sub>3</sub> and Pd<sub>8</sub>Sb<sub>3</sub> are not isostructural. Furthermore, there is no complete solid solution series Pd<sub>8</sub>As<sub>3</sub>–Pd<sub>8</sub>Sb<sub>3</sub>. The mineral Pd<sub>8</sub>As<sub>2.5</sub>Sb<sub>0.5</sub> is arsenopalladinite with triclinic symmetry, space group P $\bar{1}$  (Karimova *et al.* unpublished work). The mineral Pd<sub>8</sub>As<sub>3</sub> is stillwaterite. Its structure is still unknown. Only the trigonal system, unit-cell

parameters ( $a = 7.399$ ,  $c = 10.13$  Å) and possible space group  $P\bar{3}$  were determined (Cabri *et al.*, 1975).

The formula of the asymmetric unit of the mertieite-II structure is  $\text{Pd}_{2.67}\text{Sb}_{0.83}\text{As}_{0.17}$  ( $Z = 36$ ). It can be presented as  $\text{Pd}_{16}\text{Sb}_5\text{As}_1$  ( $Z = 6$ ), where all coefficients are integers.

$\text{Pd}_8\text{Sb}_{2.5}\text{As}_{0.5}$  ( $Z = 12$ ) is a more convenient form of the formula because the common formula of the mertieite mineral group can be represented as:  $\text{Pd}_8T1_{1.5}T2_1T3_{0.5}$ , where  $T1$ ,  $T2$  and  $T3$  are three possible positions of the Sb and As atoms in the triangular nets of the structure. Different distributions of the Sb and As atoms in these positions are possible. The  $T3$  position is completely occupied by As atoms in mertieite-II,  $\text{Pd}_8\text{Sb}_{2.5}\text{As}_{0.5}$ , and by Sb atoms in the arsenopalladinite,  $\text{Pd}_8\text{As}_{2.5}\text{Sb}_{0.5}$  (Karimova *et al.*, unpublished work). Arsenic atoms should occupy all three positions:  $T1$ ,  $T2$  and  $T3$ , in stillwaterite,  $\text{Pd}_8\text{As}_3$ . Mertieite-I, is probably a further member of the group. Its formula can be calculated on the basis of 11 atoms:  $\text{Pd}_8\text{As}_{1.5}\text{Sb}_{1.5}$ . More structural studies of stillwaterite and mertieite-I are required to check the last two hypotheses.

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