

## PLATINUM-GROUP MINERALS FROM THE WELLGREEN Ni–Cu–PGE DEPOSIT, YUKON, CANADA

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### ABSTRACT

A large variety of platinum-group minerals (PGM) are associated with base-metal sulfides in the Wellgreen Ni–Cu–PGE deposit, Yukon. Various solid-solutions occur in this deposit: (1) palladoan melonite – merenskyite – moncheite, (2) testibiopalladite – michenerite, (3) sudburyite – kotulskite – sobolevskite – (Ni,Pd)(Te,Sb,Bi)<sub>1+x</sub> (palladoan imgreite – palladoan melonite), and (4) breithauptite – sudburyite. The associated PGM and PGE-bearing phases are sperrylite, stibiopalladinite or mertieite II (or both), geversite, Pt–Pd–Fe–(Cu) alloys (Cu–Ni-rich tetraferroplatinum, and native platinum or isoferroplatinum), froodite (?), hollingworthite, laurite, native iridium, Rh-bearing cobaltite–gersdorffite, Pd-bearing ullmannite, and an unusual Re–Ir–Os–Ru alloy. The following are important characteristics of the PGM in the Wellgreen deposit: the very small grain-size of most of the PGM, unusually broad ranges of compositions of the Pd–(Pt)–Ni-rich antimonite- and bismuthotellurides, a significant extent of Ni incorporation in the Pd–(Pt) antimonite- and bismuthotellurides, and the presence of an uncommon and complex solid-solution involving sudburyite, kotulskite, sobolevskite and *Me*(Te,Sb,Bi)<sub>1+x</sub>.

*Keywords:* platinum-group elements, platinum-group minerals, antimonotellurides, bismuthotellurides, tellurides, solid solutions, mafic-ultramafic rocks, Wellgreen deposit, Quill Creek complex, Yukon, Canada.

### SOMMAIRE

Une grande variété de minéraux du groupe du platine est associée aux sulfures de métaux de base dans le gisement à Ni–Cu–EGP de Wellgreen, au Yukon. Plusieurs solutions solides sont présentes dans ce gisement: (1) melonite palladifère – merenskyite – monchéite, (2) testibiopalladite – michenerite, (3) sudburyite – kotulskite – sobolevskite – (Ni,Pd)(Te,Sb,Bi)<sub>1+x</sub> (imgreite palladifère – melonite palladifère), et (4) breithauptite – sudburyite. Les minéraux du groupe du platine et les phases porteuses des EGP incluent sperrylite, stibiopalladinite ou mertieite II (ou les deux), geversite, alliages Pt–Pd–Fe–(Cu) (tétraferroplatine enrichi en Cu–Ni, et platine natif ou isoferroplatine), froodite (?), hollingworthite, laurite, iridium natif, cobaltite–gersdorffite enrichi en Rh, ullmannite palladifère, et un alliage inhabituel contenant Re–Ir–Os–Ru. Nous résumons ici les caractéristiques importantes des minéraux du groupe du platine dans le gisement de Wellgreen: leur taille est infime dans la plupart des cas, les antimonite- et bismuthotellurures de Pd–(Pt)–Ni démontrent une grande étendue en composition, ceux-ci contiennent une proportion importante de nickel, et y est développée une solution solide complexe et non courante impliquant sudburyite, kotulskite, sobolevskite et *Me*(Te,Sb,Bi)<sub>1+x</sub>.

(Traduit par la Rédaction)

*Mots-clés:* éléments du groupe du platine, minéraux du groupe du platine, antimonotellurures, bismuthotellurures, tellurures, solutions solides, roches mafiques-ultramafiques, gisement de Wellgreen, complexe de Quill Creek, Yukon, Canada.

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## INTRODUCTION

The Wellgreen Ni–Cu–PGE (platinum-group element) deposit is situated in the Kluane district, south-western Yukon and is named after Wellington Green, who discovered this deposit in 1952, together with C.A. Aird and C.E. Hawkins. The deposit is hosted by the Quill Creek intrusive complex. This complex is Lower Triassic ( $232.3 \pm 1.0$  Ma: U–Pb dating of zircon: Mortensen & Hulbert 1991), close in age to the PGE-rich Permian–Triassic Noril'sk complex of Siberia ( $251.2 \pm 0.3$  Ma, U–Pb dating of zircon and baddeleyite: Kamo *et al.* 1996). The Wellgreen and Noril'sk deposits thus differ from most of other Ni–Cu deposits, which are Precambrian. Exploration of the Wellgreen deposit revealed reserves of 669,150 tonnes of ore, grading 2.04% Ni, 1.42% Cu, 1.3 ppm Pt, 0.93 ppm Pd, and 0.17 ppm Au (Hulbert 1997, and references therein). A relative enrichment in rarer PGE (Os, Ir, Ru, and Rh) in the sulfide ores is characteristic (Hulbert *et al.* 1988). The Wellgreen deposit was mined in 1972–73; the total production of ore was 171,652 t, with an average grade of 2.23% Ni, 1.39% Cu, 0.073% Co, 1300 ppb Pt and 920 ppb Pd (Hulbert 1997, and references therein). Various platinum-group minerals (PGM), rare minerals, and the first natural Ba-rich sulfide, owensite, have been reported from the Wellgreen deposit (Cabri *et al.* 1993, Laflamme *et al.* 1995). Our main objective here is to document the assemblages that are present. The fine grain-size and intergrowths of phases precluded identification by X-ray diffraction. We thus have relied on results of electron-microprobe analyses to identify the mineral phases. We first discuss the textural details of the phases so identified, then progress to a documentation of compositional variations and schemes of substitution. The Wellgreen suite provides unusually broad ranges of compositions of Pd–(Pt)–Ni-rich antimonotellurides and bismuthotellurides, and our work leads to some original observations concerning these economically important solid-solution series.

GEOLOGY AND BASE-METAL  
SULFIDE MINERALIZATION

The geology of the Wellgreen deposit was described by Campbell (1977), Hulbert *et al.* (1988), Cabri *et al.* (1993), Miller (1991), and Hulbert (1997). The Quill Creek ultramafic-mafic complex, which hosts the deposit, is about 16 km long and 0.6 km thick. The intrusion is located at the boundary between the Lower Permian volcanic and sedimentary rocks of the Station Creek Formation and the Permian sedimentary rocks and limestone of the Hasen Creek Formation. The Wellgreen sill is about 5 km long; it is located in the thickest part of the complex and consists of dunite, wehrlite, clinopyroxenite, olivine clinopyroxenite, gabbro, and massive sulfides (Hulbert *et al.* 1988, Miller 1991, Hulbert 1997).

Various zones of base-metal sulfides (BMS) are associated with the Wellgreen sill: (1) massive sulfide lenses, 2 to 6 m in thickness, at the contact between the gabbro and overlying country-rock, (2) the BMS in gabbro, (3) the BMS in olivine clinopyroxenite and wehrlite, and (4) the BMS in footwall country-rock (Hulbert *et al.* 1988, Cabri *et al.* 1993, Hulbert 1997).

According to the existing model, a basaltic parental magma was responsible for the Wellgreen sill; it was enriched in the PGE, and initially undersaturated with respect to sulfides (Hulbert *et al.* 1988, Miller 1991, Marcantonio *et al.* 1994, Hulbert 1997). Rapid cooling, decompression and crystallization of this magma upon intrusion provoked saturation and separation of droplets of an immiscible sulfide liquid. These droplets scavenged the PGE and coalesced at the bottom to form lenses of the PGE-rich massive sulfide ore. Anomalous concentrations of Ba and the presence of Ba-rich minerals (such as barite and owensite), locally developed in the sill, could be related to a magmatic contamination from Ba-rich sediments, or to a post-crystallization alteration of the sill rocks by hydrothermal fluids that had equilibrated with the surrounding sedimentary rocks (Cabri *et al.* 1993, Marcantonio *et al.* 1994, Laflamme *et al.* 1995).

THE DISTRIBUTION OF PLATINUM-GROUP  
MINERALS AND PGE-RICH PHASES

The PGM were examined in heavy-mineral concentrates, obtained from samples representative of various PGE-rich zones of the complex (Table 1). More than one thousand two hundred individual grains of various PGM and PGE-bearing minerals were identified on the basis of a careful optical examination and electron-microprobe analyses (*e.g.*, Figs. 1A–F, 2A–F).

About half of the grains of PGM consist of sperrylite (PtAs<sub>2</sub>); the rest is made up of sudburyite [(Pd,Ni)Sb] (18%), merenskyite [(Pd,Pt,Ni)(Te,Bi)<sub>2</sub>] (8%), moncheite [(Pt,Pd,Ni)(Te,Bi)<sub>2</sub>] (6%), testibiopalladite [Pd(Sb,Bi)Te] and michenerite [Pd(Bi,Sb)Te] (5% each), kotulskite [Pd(Te,Bi,Sb)] (2%), stibiopalladinite (Pd<sub>5</sub>Sb<sub>2</sub>) or mertieite II (Pd<sub>8</sub>Sb<sub>3</sub>) (or both) (2%), and less than 1% each are the other PGM: (Pd,Ni)(Te,Sb,Bi)<sub>1+x</sub>-type phases, geversite [Pt(Sb,Bi)<sub>2</sub>], Pt–Pd–Fe–(Cu) alloys, froodite (PdBi<sub>2</sub>), hollingworthite (RhAsS), laurite [(Ru,Os)S<sub>2</sub>], and native Ir.

In order of decreasing abundance, the PGE-bearing minerals are palladoan melonite [(Ni,Pd,Pt)(Te,Bi)<sub>2</sub>], (Ni,Pd)(Te,Sb,Bi)<sub>1+x</sub>-type phases, palladoan breithauptite [(Ni,Pd)Sb], palladoan imgreite or hexatestibiopannickelite [(Ni,Pd)(Te,Sb)], Pd-bearing ullmannite (NiSbS), rhodian cobaltite [(Co,Ni,Rh)AsS], and an unusual Re–Ir–Os–Ru alloy. In addition, trace levels of Pd, Rh and Ru were detected in some of the BMS (Cabri *et al.* 1993).

TABLE 1. SAMPLES USED IN THIS STUDY OF THE PLATINUM-GROUP MINERALS IN THE WELLGREEN DEPOSIT, YUKON

Sample	Description <sup>§</sup>
A Massive sulfide ore, East Zone	Main opaque minerals: pyrrhotite and pentlandite, followed by chalcopyrite, pyrite, and magnetite. Minor and rare minerals: cobaltite – gersdorffite, arsenopyrite, ullmannite, chromite, violarite, galena, Au–Ag alloy, and altaite.
B Semi-massive sulfides in a chilled gabbro, East Zone	Opaque minerals are the same as those listed for sample A.
D-1 Disseminated sulfides in wehrlite, West Zone	Main opaque minerals: pyrrhotite and pentlandite, followed by chalcopyrite, and magnetite. Minor and rare minerals: pyrite, cobaltite – gersdorffite, owensite*, arsenopyrite, ilmenite, chromite, galena, hessite, Au–Ag alloy, and argentopentlandite.
E-1 Disseminated sulfides in a chilled gabbro and associated pegmatitic gabbro, West Zone	Main opaque minerals: chalcopyrite, pyrite, pyrrhotite, ilmenite, and pentlandite. Minor and rare minerals: violarite, cobaltite – gersdorffite, argentopentlandite, sphalerite, siegenite, Bi telluride(s), altaite, matildite (?), galena, covellite, Au–Ag alloy, and hessite.
E-2 Disseminated sulfides in a chilled gabbro and associated pegmatitic gabbro, West Zone	Main opaque minerals: pyrrhotite and pentlandite. Minor and rare minerals: pyrite, cobaltite – gersdorffite, arsenopyrite, ullmannite, chalcopyrite, nickeline, violarite, chromite, sphalerite, magnetite, argentopentlandite, breithauptite, covellite, marcasite, galena, rutile, Au–Ag alloy, and owensite*.
#1 Sulfide-bearing gabbro, West Zone	Main opaque minerals: chalcopyrite, pentlandite, pyrrhotite, ilmenite, and pyrite. Minor and rare minerals: barite, chromite, magnetite, cobaltite – gersdorffite, arsenopyrite, siegenite, violarite, titanite, argentopentlandite, galena, altaite, hessite, and Au–Ag alloy.
#2 Sulfide-bearing clinopyroxenite, West Zone	Main opaque minerals: chalcopyrite, ilmenite, magnetite, pentlandite, and violarite. Minor and rare minerals: pyrite, chromite, pyrrhotite, sphalerite, barite, arsenopyrite, cobaltite – gersdorffite, argentopentlandite, galena, altaite, breithauptite, hessite, and Au–Ag alloy.
#3 Sulfide-bearing wehrlite, East Zone.	Main opaque minerals: chalcopyrite, pyrrhotite, and magnetite. Minor and rare minerals: pentlandite, violarite, pyrite, chromite, ilmenite, sphalerite, barite, arsenopyrite, cobaltite – gersdorffite, covellite, galena, ullmannite, and Au–Ag alloy.

<sup>§</sup> After Cabri *et al.* (1993). \* (Ba,Pb)<sub>6</sub>(Cu,Fe,Ni)<sub>25</sub>S<sub>27</sub> (Laflamme *et al.* 1995).

### Sperrylite

The mode of occurrence of sperrylite varies from one Ni–Cu–PGE zone to another. In sample A, sperrylite ranges in size between  $6 \times 10$  to  $12 \times 30 \mu\text{m}$  (six grains) and forms subhedral inclusions in pyrrhotite and, rarely, in pentlandite. Intergrowths of sperrylite with merenskyite–moncheite were observed. In sample B, sperrylite occurs as larger grains, varying between  $15 \times 75$  and  $70 \times 100 \mu\text{m}$ . Nine grains of sperrylite (subhedral to euhedral) were found. They display intergrowth relationships with chalcopyrite, and one of these grains is intergrown with testibiopalladite and a

silicate mineral. In sample D–1, eighty-six grains of sperrylite were found; they are anhedral or subhedral to euhedral, and vary from  $<2 \mu\text{m}$  to  $30 \times 65 \mu\text{m}$ . Of these grains, 66% occur in magnetite, 29% in chalcopyrite, 5% in pyrrhotite and 1% in silicate minerals. Intergrowths of sperrylite with sudburyite, michenerite and kotulskite were observed. A total of one hundred and eighty-seven grains of sperrylite, euhedral to subhedral ( $5 \times 10$  to  $145 \times 145 \mu\text{m}$ ), were found in sample E–1, in which sperrylite is the only observed mineral of Pt. The grains commonly contain inclusions of chalcopyrite, hessite, a Bi telluride, froodite(?) and Au–Ag alloy. In the fractions examined under microscope, about 40% of the sperrylite grains contain inclusions of chalcopyrite, or are in contact with it; fewer grains (10.5%) are closely associated with silicate minerals or ilmenite. In contrast, in sample E–2, nearly all (99%) of the twenty-one grains of sperrylite (anhedral to subhedral,  $<2$  to  $40 \times 55 \mu\text{m}$ ), were found in association with silicate minerals, and only 1% of these grains are associated with pyrrhotite. In sample #1, sperrylite is the only Pt mineral observed in association with pyrrhotite and chalcopyrite. The grains of sperrylite are mostly anhedral ( $<2$  to *ca.*  $60 \mu\text{m}$ ), but a few euhedral grains also were encountered.

### Sudburyite

Sudburyite is relatively common in all of the samples studied. In sample A, twenty-eight grains of sudburyite were found; these are present as tiny inclusions,  $<2$  to  $3 \times 6 \mu\text{m}$ , in pyrrhotite (94% of the grains) and cobaltite (6%). In sample B, seven anhedral grains of sudburyite (up to  $6 \mu\text{m}$  across) occur as inclusions in arsenide and sulfarsenide minerals (63% in nickeline and 37% in cobaltite–gersdorffite). A similar pattern of distribution of sudburyite was previously reported from Sudbury (Cabri & Laflamme 1976). In sample D–1, sudburyite is more abundant: seventy-one grains were observed (up to  $60 \mu\text{m}$ ) in association with silicate minerals (79%), magnetite (14%), chalcopyrite (5%) and pyrrhotite (1%). The sudburyite is mostly anhedral, commonly intergrown with sperrylite, kotulskite, michenerite and Au–Ag alloy. A tiny inclusion of sudburyite ( $2 \times 3 \mu\text{m}$ ) in sperrylite was found in sample E–1, and four inclusions (up to  $5 \mu\text{m}$ ) of sudburyite were found in cobaltite–gersdorffite and ullmannite in sample E–2. A single inclusion of sudburyite ( $2 \times 3 \mu\text{m}$ ) was found in sample #1, and forty-seven grains (up to  $8 \times 13 \mu\text{m}$ ), anhedral or subhedral, were observed as inclusions in chalcopyrite (58% of the grains), magnetite (24%), pentlandite (9%), pyrrhotite (2%) and in silicate minerals (7%). In addition, sudburyite in sample #1 also commonly occurs at the contact between the BMS and magnetite. In sample #3, twenty-six grains of sudburyite were found; these range from  $<2$  to  $4 \times 6 \mu\text{m}$  and commonly occur as euhedral (or anhedral to subhedral) inclusions in pentlandite. Thirty-six percent of sudburyite grains were

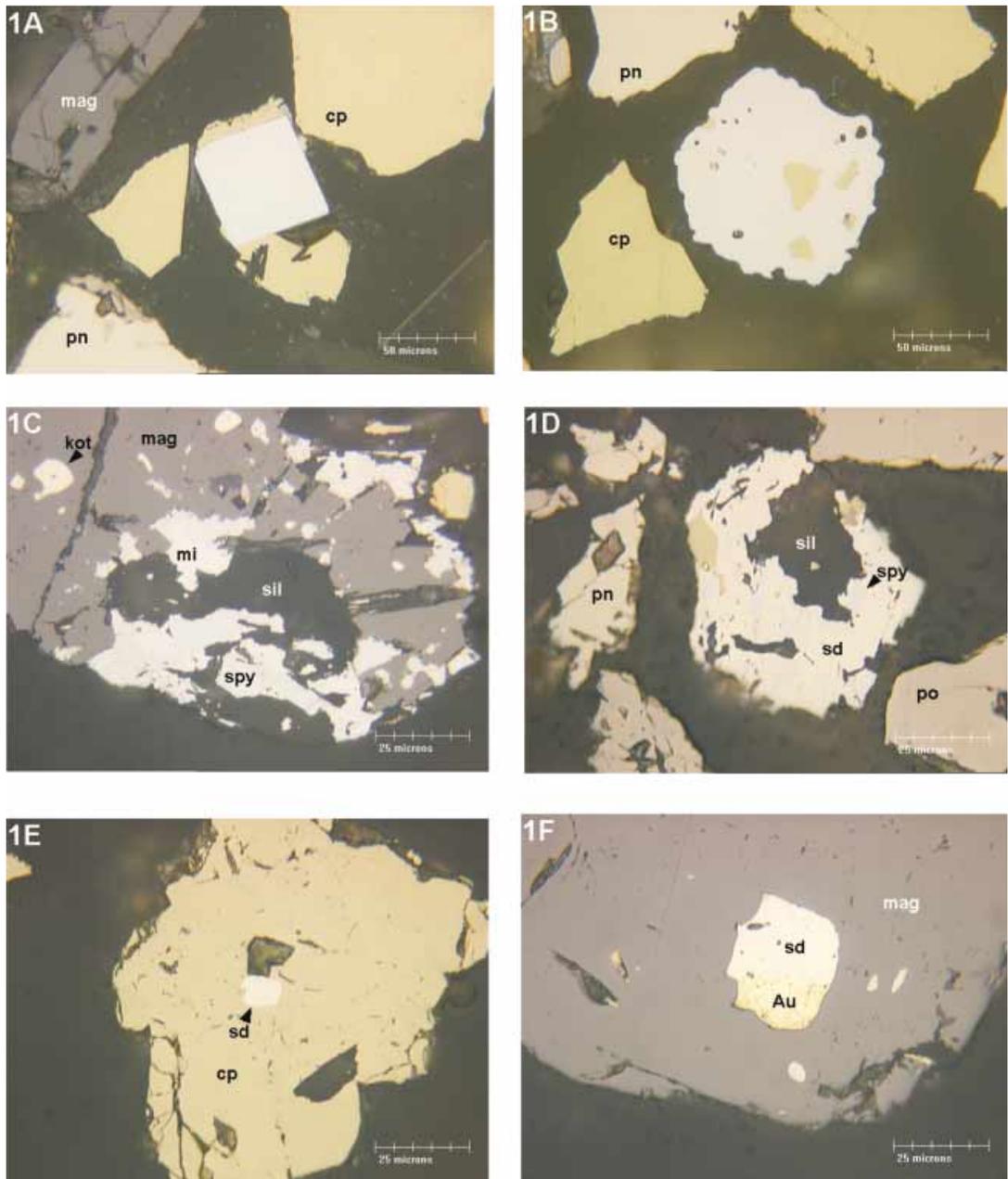


FIG. 1. Euhedral (1A) and anhedral (1B) grains of sperrylite (bluish white) in association with chalcopyrite (cp), pentlandite (pn), and magnetite (mag). C. Sperrylite (spy) and michenerite (mi) intergrown with a silicate mineral (sil) and magnetite (mag), which also contains an inclusion of kotulskite (kot). D-F. Sudburyite (sd) associated with sperrylite (spy), chalcopyrite (cp), magnetite (mag), and Au-Ag alloy (Au). Additional symbol: po: pyrrhotite.

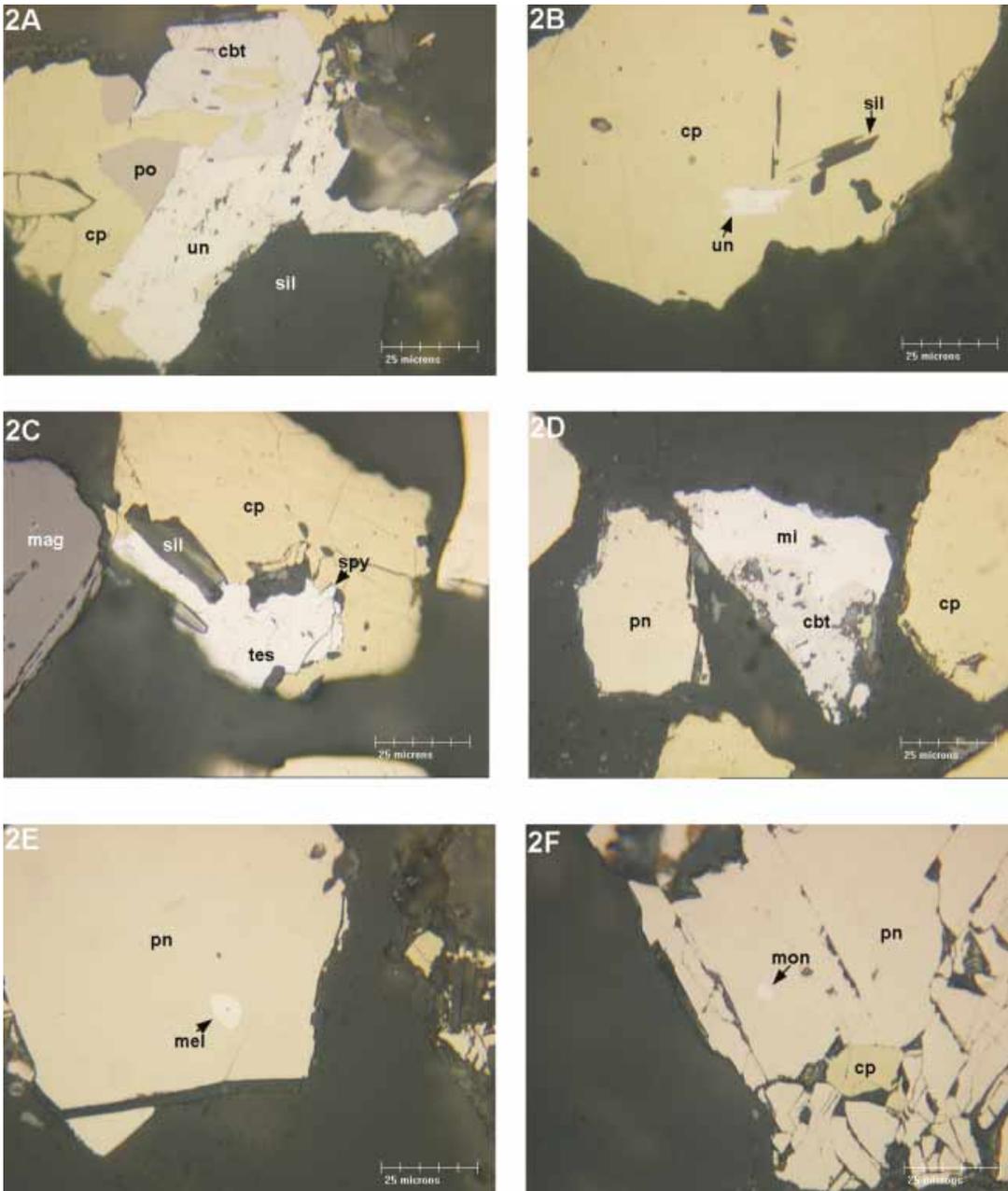


FIG. 2. A and B. Phases  $Me(\text{Te,Sb,Bi})_{1+x}$  (un) associated with chalcopyrite (cp), pyrrhotite (po), cobaltite-gersdorffite (cbt), and a silicate mineral (sil). C. Grain of testibiopalladite (tes), which is enclosed by chalcopyrite (cp) and contains micro-inclusions of sperrylite (spy). Symbols: sil: silicate mineral, mag: magnetite. D. Intergrowth of michenerite (mi) with cobaltite-gersdorffite (cbt). Additional symbol: pn: pentlandite. E and F. Micro-inclusions of palladoan melonite (mel) and moncheite (mon) in pentlandite (pn).

observed as inclusions within pentlandite or violarite, 30% within pyrrhotite, 19.8% within chalcopyrite, and 13.8% are associated with magnetite.

#### *Kotulskite*

Kotulskite was observed only in sample D-1, in which seventeen subhedral to euhedral grains (<1 to 10  $\mu\text{m}$ ) were found as inclusions in magnetite. Kotulskite also occurs as a polymineralic intergrowth that contains sperrylite, sudburyite and pyrrhotite.

#### *Sobolevskite – (kotulskite)*

Three anhedral grains (up to  $5 \times 15 \mu\text{m}$ ) of sobolevskite–kotulskite solid solution were found in sample D-1 in association with silicate minerals, sperrylite, sudburyite and chalcopyrite.

#### *Phases of the type (Pd,Ni)(Te,Sb,Bi)<sub>1+x</sub>*

Various phases of the type (Pd,Ni)(Te,Sb,Bi)<sub>1+x</sub> [or (Pd,Ni)<sub>1-x</sub>(Te,Sb,Bi)], either Pd-dominant or Ni-dominant (see below), occur as tiny grains (predominantly  $\leq 2$  to 10  $\mu\text{m}$ ), which consist of single phases, in contrast to fine-scale intergrowths reported from the Stillwater complex (Cabri & Pickwick 1974). In sample D-1, the phase (Pd,Ni)(Te,Sb,Bi)<sub>1+x</sub> is present as inclusions in pyrrhotite and displays intergrowth relationship with sudburyite and sperrylite. A larger intergrowth of this phase (12  $\times$  40  $\mu\text{m}$ ) with michenerite is enclosed by magnetite. In sample #2, the phase was observed as an intergrowth with altaite at a chalcopyrite–magnetite contact, and also as tiny inclusions in chalcopyrite and pentlandite. In sample E-2, a phase of this type was observed as an inclusion (2  $\times$  5  $\mu\text{m}$ ) in pyrrhotite. In sample #1, two grains of the antimonotelluride (Pd,Ni)(Te,Sb,Bi)<sub>1+x</sub> were found as tiny inclusions in pyrrhotite and pentlandite.

#### *Phases of the type (Ni,Pd)(Te,Sb,Bi)<sub>1+x</sub>*

Phases of the type (Ni,Pd)(Te,Sb,Bi)<sub>1+x</sub> [or (Ni,Pd)<sub>1-x</sub>(Te,Sb,Bi)] are among the most common PGE-bearing minerals at Wellgreen. As in the case of the (Pd,Ni)(Te,Sb,Bi)<sub>1+x</sub> phases, these antimonotellurides display considerable variations in the ratio (Pd + Pt + Ni) : (Te + Sb + Bi), which is commonly close to 2 : 3 or 3 : 4. A total of one hundred and seventeen grains of the phase (Ni,Pd)<sub>2</sub>(Te,Sb)<sub>3</sub> were identified, which are mostly euhedral to subhedral, and rarely anhedral. In sample B, two tiny inclusions (2 to 3  $\mu\text{m}$ ) of this phase were observed in pentlandite and pyrrhotite. In sample E-2, thirty-three grains of this phase were found; they are enclosed by pyrrhotite (81% of the grains) or are associated with both pyrrhotite and cobaltite–gersdorffite (19%). In sample #1, sixty-five grains were found (<2 to 25  $\times$  80  $\mu\text{m}$ ); they are associated with chalcopyrite

(87.8%), pyrrhotite (7.7%) and pentlandite (4.5%). In sample #2, seventeen grains (<2 to 12  $\times$  20  $\mu\text{m}$ ) were identified; they are hosted by magnetite (85.1%), pentlandite (10.7%) and chalcopyrite (4.2%).

The similar phase (Ni,Pd)<sub>3</sub>(Te,Sb)<sub>4</sub> also occurs as tiny, commonly euhedral grains. In sample E-2, two inclusions of this phase were found in pyrrhotite ( $\leq 7 \mu\text{m}$ ), and one inclusion (10  $\mu\text{m}$ ) was found in cobaltite–gersdorffite. In sample #2, sixteen grains were identified (<2 to 5  $\times$  10  $\mu\text{m}$ ); they are enclosed by chalcopyrite (61.2% of the grains), pentlandite (20.7%) magnetite (12%) and pyrrhotite (6.1%). In sample #3, twenty grains (<1 to 4  $\times$  6  $\mu\text{m}$ ) were observed as inclusions in pyrrhotite (32.9%), chalcopyrite (30.3%), pentlandite and violarite replacing this pentlandite (27.3%), and magnetite (9.6%).

#### *Testibiopalladite*

In sample A, seven subhedral grains of testibiopalladite (<2 to 6  $\times$  14  $\mu\text{m}$ ), all of which are included in pyrrhotite, were found. In sample B, eleven subhedral grains (up to 15  $\mu\text{m}$ ) were observed. They are mostly associated with pyrrhotite; one of these grains forms an inclusion in chalcopyrite and is associated with sperrylite. In sample E-1, four grains were observed; they range from 5  $\times$  15 to 18  $\times$  35  $\mu\text{m}$ . Two of these grains are anhedral, and are associated with ilmenite and chalcopyrite and with sperrylite and chalcopyrite, respectively. The other two grains (anhedral and euhedral) are enclosed by chalcopyrite. In sample E-2, four anhedral or subhedral grains of testibiopalladite (3 to 6  $\times$  10  $\mu\text{m}$ ) were observed in association with cobaltite–gersdorffite and pyrrhotite. In sample #1, twenty-two grains were found (<2 to 20  $\times$  25  $\mu\text{m}$ ). They are commonly subhedral, mostly occur as inclusions in chalcopyrite (91%), pyrrhotite (6%) and pentlandite (3%), and may form intergrowths with sperrylite and the (Ni,Pd)(Te,Sb,Bi)<sub>1+x</sub>-type phases. Two tiny grains of testibiopalladite were encountered in sample #2. These are anhedral; one grain is intergrown with sudburyite and is enclosed by pentlandite, and the second is intergrown with hessite and is enclosed by chalcopyrite.

#### *Michenerite*

In sample D-1, michenerite (3  $\times$  10 to 15  $\times$  25  $\mu\text{m}$ ) is closely associated with magnetite or hydrous silicates of the serpentine group and subordinate magnesian calcic amphibole, and commonly occurs in a complex intergrowth with other PGM, commonly sperrylite and sudburyite. Two tiny inclusions (2  $\times$  4 and 6  $\times$  6  $\mu\text{m}$ ) of michenerite were also observed in pyrrhotite. In sample E-1, ten grains (mostly anhedral: 2  $\times$  3 to 20  $\times$  55  $\mu\text{m}$ ) were found in association with cobaltite–gersdorffite (74% of the grains), chalcopyrite (24%), violarite and silicate minerals (1% each). In sample #1, ten anhedral grains of michenerite were observed (<2 to

9 × 11 μm) as inclusions in pyrrhotite and chalcopyrite (74 and 1%, respectively) and as intergrowths with euhedral cobaltite–gersdorffite (25%). In sample #2, nineteen grains of michenerite (commonly irregular: <2 to 8 × 21 μm) were observed in association with pentlandite (73% of the grains), chalcopyrite (10%) and silicate minerals (3%). Commonly, such michenerite occurs in a complex intergrowth with other PGM (sudburyite, sperrylite, *etc.*) or hessite.

#### *Palladoan melonite*

In general, members of the melonite series are among the most common PGE-rich minerals at Wellgreen; seventy-four grains (predominantly anhedral) were found. In samples A and B, three and one inclusions of melonite, respectively, were found in pyrrhotite. Thirty-one grains of melonite (<2 to 20 μm) were found in sample E-1, and nineteen grains (<2 to 5 × 8 μm) were found in sample E-2. In the samples E-1 and E-2, respectively, the melonite grains are enclosed by pyrrhotite (86 and 97.2%), sperrylite (10.8 and 0%), chalcopyrite (2.2 and 0%), pentlandite (0 and 2.5%), pyrite (1 and 0%), and cobaltite–gersdorffite (0 and 0.3%). In sample #1, fourteen grains were found (<2 to 10 μm); they are enclosed by pentlandite (54.7%), pyrrhotite (44.7%) and chalcopyrite (0.6%). In sample #2, five tiny grains (up to 3 × 5 μm) were identified, three of which are inclusions in pentlandite, and the two other are enclosed by pyrrhotite and chalcopyrite. In sample #3, a single euhedral grain of melonite was found in association with pyrrhotite.

#### *Merenskyite*

Merenskyite is the most common mineral of Pd in sample A; seventy-two grains (predominantly subhedral to euhedral) were found. They vary from <2 to 10 × 15 μm and mostly occur as inclusions in pyrrhotite (85% of the grains), pentlandite (15%) and chalcopyrite (<1%). In sample B, two tiny euhedral grains of merenskyite (1 × 2 and 3 μm) were observed as inclusions in pyrrhotite.

#### *Moncheite*

In terms of relative abundance, moncheite is quite common at Wellgreen. It is extremely fine-grained, and the grains rarely exceed 5 μm. In sample A, thirty-three grains of moncheite (<2 to 4 × 5 μm) were found; they occur as inclusions in pyrrhotite (85% of the grains), pentlandite (12%) and chalcopyrite (3%). In sample B, a single grain (4 × 6 μm) only was found, included in pyrrhotite. A total of twenty-nine grains were found in sample D-1, in which they occur as inclusions, from <2 to 5 × 10 μm in size, in pyrrhotite (90% of the grains), magnetite (9%) and chalcopyrite (1%). In sample #2, a single inclusion (2 × 4 μm) of moncheite was observed, in magnetite.

#### *Stibiopalladinite or mertieite II*

Tiny grains of stibiopalladinite (or mertieite, or both) are commonly present as anhedral inclusions in magnetite. In association with magnetite, eighteen grains (<1 to 4 × 11 μm) of stibiopalladinite were found in sample D-1, and two grains (<5 μm across) were found in sample #2. In sample #3, three tiny grains of stibiopalladinite (≤7 μm) were found in association with pentlandite, which is replaced by violarite and magnetite.

#### *Pd-rich breithauptite*

Breithauptite is rare. Several grains of breithauptite were observed in sample E-2. They are anhedral, less than 40 μm across, and typically are associated with cobaltite–gersdorffite, ullmannite and chalcopyrite. In sample #2, Pd-bearing breithauptite occurs as subhedral tiny grains (3 × 6 to 8 × 10 μm), associated with chalcopyrite, magnetite and pentlandite.

#### *Pd-rich ingreite or hexatestibiopanickelite*

A submicrometric inclusion (*ca.* 2 μm) of Pd-bearing ingreite (or hexatestibiopanickelite) was found in pyrrhotite in sample E-2.

#### *Froodite (?)*

Two tiny inclusions (2 × 2 and 2 × 3 μm) of a Pd-rich bismuthide, probably froodite (PdBi<sub>2</sub>; Cabri *et al.* 1973), were encountered in sperrylite in sample E-1. Owing to the small grain-size, this grain could not be analyzed quantitatively.

#### *Geversite*

In samples B and #2, two grains of geversite (up to 2 × 3 μm) were found as inclusions in pyrrhotite and pentlandite. In addition, geversite was observed in sample D-1 as a microsymplectitic intergrowth (6 × 8 μm) with magnetite.

#### *Pt–Pd–Fe–(Cu) alloys*

In sample #2, four tiny grains (up to 4 μm) of Pt–Fe alloy were found. They are subhedral to euhedral, are associated with pentlandite or chalcopyrite, and are enclosed by magnetite. A euhedral crystal of Pt–Fe alloy also forms part of a polyminerale intergrowth that consists of sperrylite, an undefined Ni arsenide, and a Mg–Fe aluminosilicate.

#### *Hollingworthite*

Four tiny grains of a PGE sulfarsenide, probably hollingworthite [(Rh>Ir>Pt)AsS], were qualitatively identified by EDS spectrometry in samples 1 and 2: (1)

<2  $\mu\text{m}$  inclusion in cobaltite, enclosed by pentlandite (sample #1), (2) a  $2 \times 4 \mu\text{m}$  grain surrounded by a silicate; this grain forms a complex intergrowth with sperrylite, sudburyite and an Ir-rich phase, (3) a  $1 \times 12 \mu\text{m}$  grain, intergrowth with laurite within magnetite, and (4) a  $3 \times 3 \mu\text{m}$  inclusion in magnetite from sample #2.

#### Laurite

Two tiny grains of laurite,  $(\text{Ru} > \text{Ir} > \text{Os})(\text{S} > \text{As})_2$ , were identified by EDS spectrometry in sample #2. The first grain ( $1 \times 2 \mu\text{m}$ ) is located in magnetite, and the second grain ( $2 \times 3 \mu\text{m}$ ) is associated with hollingworthite, and these are hosted by magnetite.

#### Rh-bearing cobaltite-gersdorffite

In samples E-2 and #1, euhedral to subhedral crystals of cobaltite-gersdorffite are enclosed by pyrrhotite and pentlandite and contain tiny zones enriched in Rh and, to a lesser extent, in Ir. The maximum content of Rh (2.7 wt.%) was detected in a minute grain of cobaltite ( $1 \times 3 \mu\text{m}$ ), enclosed by pyrrhotite, in sample #1.

#### Native Ir

A single grain of native Ir (*ca.*  $0.5 \times 3 \mu\text{m}$ ) was identified as a complex intergrowth with sperrylite,

sudburyite, and hollingworthite within a silicate (sample #2).

#### Re-PGE-rich alloy

A complex alloy ( $\text{Re} > \text{Ir} > \text{Os} > \text{Ru}$ ) occurs as a tiny grain ( $2 \times 2 \mu\text{m}$ ), enclosed by a euhedral grain of cobaltite associated with chalcopyrite in sample #1. The presence of Re was carefully checked by WDS spectrometry.

#### ANALYTICAL METHODS

Owing to the very fine grain-size of most of the PGM, the bulk of the analyses were done by energy-dispersion spectrometry (EDS) in order to minimize interference caused by the beam overlap onto surrounding minerals. In the case of the presence of pentlandite in contact with the analyzed PGM, equivalent amounts of Fe, Ni, and S were subtracted from the analytical results. All the analyses that gave totals of  $100 \pm 2.5 \text{ wt.}\%$ , were normalized to 100 wt.%. The EDS analyses were carried out at an accelerating voltage of 20 kV and a beam current (Faraday cup reading) of 10 nA. The counting times were 100 s, and the following X-ray lines and standards were used:  $\text{PdL}\alpha$ ,  $\text{NiK}\alpha$ ,  $\text{PtM}\alpha$ ,  $\text{FeK}\alpha$ ,  $\text{CoK}\alpha$ ,  $\text{TeL}\alpha$ ,  $\text{SbL}\alpha$ ,  $\text{BiM}\alpha$  (pure elements), and  $\text{AsL}\alpha$  (synthetic InAs). The raw data were corrected on-line, using the Tracor Northern's ZAF program.

The wavelength-dispersion electron-microprobe analyses (WDS) were carried out with a JEOL-733 instrument at an accelerating voltage of 20 kV and a beam current of 20 nA. The counting times were 10 to 100 s. The following X-ray lines (and standards) were used. (1) For sperrylite:  $\text{PtL}\alpha$  and  $\text{AsK}\alpha$  (synthetic  $\text{PtAs}_2$ ),  $\text{OsL}\alpha$ ,  $\text{IrL}\alpha$ ,  $\text{RuL}\alpha$ ,  $\text{RhL}\alpha$ ,  $\text{PdL}\alpha$  (pure metals), and  $\text{SK}\alpha$  (pyrite). (2) For breithauptite:  $\text{NiK}\alpha$  and  $\text{SbL}\alpha$  (synthetic NiSb),  $\text{CoK}\alpha$  and  $\text{SK}\alpha$  (synthetic  $\text{CoSbS}$ ),  $\text{AsL}\alpha$  (synthetic InAs),  $\text{FeK}\alpha$ ,  $\text{TeL}\alpha$ ,  $\text{PdL}\alpha$ , and  $\text{PtL}\alpha$  (pure metals). (3) For ullmannite:  $\text{NiK}\alpha$  (synthetic NiSb),  $\text{CoK}\alpha$ ,  $\text{SbL}\alpha$ ,  $\text{SK}\alpha$  (synthetic  $\text{CoSbS}$ ),  $\text{AsL}\alpha$  (synthetic InAs),  $\text{FeK}\alpha$ ,  $\text{PdL}\alpha$ , and  $\text{PtL}\alpha$  (pure metals).

#### COMPOSITIONAL VARIATIONS

##### Sperrylite

As in the case of most occurrences of sperrylite (Cabri & Laflamme 1981), the composition of sperrylite at Wellgreen is close to stoichiometric  $\text{PtAs}_2$  (Table 2). Sb may be present at a substantial level (up to 2.5 wt.%; 0.07 atoms per formula unit, *apfu*), consistent with the existence of an extensive solid-solution between sperrylite and geversite (Johan *et al.* 1989). Concentrations of Ir (0.2 wt.%) and Os (0.1 wt.%) are invariably minor in sperrylite from Wellgreen.

TABLE 2. COMPOSITION OF SPERRYLITE FROM THE WELLGREEN Ni-Cu-PGE DEPOSIT

No.	Pt	Ir	Os	As	Sb	Total	
1 wt.%	56.6	0.23	0.11	41.1	2.5	100.54	
2	57.1	0.13	0.09	42.6	1.0	100.92	
3	57.1	n.d.	n.d.	41.7	1.6	100.40	
4	57.7	n.d.	n.d.	42.8	0.40	100.90	
5	56.1	n.d.	n.d.	42.2	0.94	99.24	
6	57.0	n.d.	n.d.	42.6	1.1	100.70	
7	56.6	n.d.	n.d.	41.8	1.5	99.90	
8	57.0	n.d.	n.d.	43.4	0.68	101.08	
9	56.8	n.d.	0.13	42.9	0.96	100.79	
10	56.9	n.d.	n.d.	43.4	0.33	100.63	
	Pt	Ir	Os	$\Sigma\text{Me}$	As	Sb	As+Sb
1 <i>apfu</i>	1.01	<0.01	<0.01	1.02	1.91	0.07	1.98
2	1.01	<0.01	<0.01	1.01	1.96	0.03	1.99
3	1.02	—	—	1.02	1.94	0.05	1.99
4	1.02	—	—	1.02	1.97	0.01	1.98
5	1.00	—	—	1.00	1.97	0.03	2.00
6	1.01	—	—	1.01	1.96	0.03	1.99
7	1.01	—	—	1.01	1.95	0.04	1.99
8	1.00	—	—	1.00	1.98	0.02	2.00
9	1.00	—	<0.01	1.00	1.97	0.03	2.00
10	1.00	—	—	1.00	1.99	0.01	2.00

<sup>§</sup> Results of WDS electron-microprobe analyses. n.d.: not detected. Ru, Rh, Pd and S were sought, but not detected. The minimum detection limits are 0.07 wt.% for Os and 0.08 wt.% for Ir. The atomic proportions are based on three atoms per formula unit (*apfu*).

*Solid solution of sudburyite, kotulskite, sobolevskite and Me(Te,Sb,Bi)<sub>1+x</sub>*

An extensive solid-solution involving sudburyite, kotulskite and sobolevskite (Tables 3, 4, Fig. 3) is present at Wellgreen. In addition, phases of the type (Pd,Ni)(Te,Sb,Bi)<sub>1+x</sub> and (Ni,Pd)(Te,Sb,Bi)<sub>1+x</sub> display clear compositional similarities also with members of the sudburyite – kotulskite – (sobolevskite) series. Compositions are projected onto the Te–Bi–Sb ternary (Fig. 3). The phases show a relative excess in the content of semimetals (or a deficit in the content of metals), and the observed ratio (Pd + Pt + Ni) : (Te + Sb + Bi) of these phases varies considerably, being close to 3 : 4 (*i.e.*, 0.75), 2 : 3 (0.67) or 3 : 5 (0.60) (Table 5). On a plot of a total of semimetals *versus* a total of metals, compositions of sudburyite – kotulskite – sobolevskite and of the phases *Me(Te,Sb,Bi)<sub>1+x</sub>* extend along a linear trend to form an extensive solid-solution series (Fig. 4). Most members of this series display a relative excess in the content of semimetals, and only a few of the mem-

TABLE 4. COMPOSITION OF KOTULSKITE – (SUDBURYITE) – SOBOLEVSKITE FROM THE WELLGREEN Ni–Cu–PGE DEPOSIT

No.	Pd	Ni	Pt	Sb	Te	Bi	Total	
1 wt%	39.6	0.62	0.31	14.7	25.2	18.7	99.13	
2	38.9	0.23	0.19	11.1	27.8	21.7	99.92	
3	38.8	0.80	0.27	10.2	27.4	23.1	100.57	
4	38.3	0.46	0.27	5.1	28.8	27.1	100.03	
5	36.1	0.38	n.d.	4.9	20.3	37.3	98.98	
	Pd	Ni	Pt	ΣMe	Sb	Te	Bi	Σ
1 <i>apfu</i>	0.94	0.03	<0.01	0.97	0.30	0.50	0.23	1.03
2	0.93	0.01	<0.01	0.94	0.23	0.56	0.27	1.06
3	0.92	0.03	<0.01	0.95	0.21	0.54	0.28	1.03
4	0.94	0.02	<0.01	0.96	0.11	0.59	0.34	1.04
5	0.94	0.02	–	0.96	0.11	0.44	0.49	1.04

Results of EDS electron-microprobe analyses (listed in order of increasing content of Bi) of kotulskite – (sudburyite) – sobolevskite grains enclosed by magnetite. n.d.: not detected. The atomic proportions are based on two atoms per formula unit (*apfu*).

TABLE 5. COMPOSITION OF *Me(Te,Sb,Bi)<sub>1+x</sub>*-TYPE PHASES FROM THE WELLGREEN Ni–Cu–PGE DEPOSIT

No.	Pd	Ni	Pt	Sb	Te	Bi	Total	
1 wt%	30.4	5.9	0.12	33.5	19.9	9.9	99.72	
2	28.0	6.4	n.d.	26.9	34.4	3.2	98.90	
3	25.0	8.7	0.52	28.0	37.7	n.d.	99.92	
4	17.5	10.5	0.37	17.7	52.1	n.d.	98.17	
5	16.6	11.1	0.28	15.4	53.6	1.4	98.38	
6	14.9	12.7	n.d.	14.6	56.8	1.0	100.00	
7	12.8	13.9	n.d.	13.9	58.9	0.63	100.13	
8	15.2	14.8	n.d.	30.6	39.4	n.d.	100.00	
9	15.9	15.2	n.d.	31.7	37.2	n.d.	100.00	
10	14.4	16.0	0.42	29.7	36.5	3.0	100.02	
11	9.7	17.0	0.35	22.7	49.5	n.d.	99.25	
12	6.6	18.4	0.16	21.6	51.5	0.71	98.97	
13	6.5	19.1	0.15	22.0	51.3	n.d.	99.05	
14	5.8	19.7	n.d.	23.2	51.2	n.d.	99.90	
15	5.9	20.1	n.d.	23.0	51.1	n.d.	100.10	
16	5.5	20.3	n.d.	22.9	50.9	n.d.	99.99	
	Pd	Ni	Pt	ΣMe	Sb	Te	Bi	Σ
1 <i>apfu</i>	0.66	0.23	<0.01	0.89	0.64	0.36	0.11	1.11
2	0.60	0.25	–	0.85	0.50	0.61	0.03	1.14
3	0.52	0.33	<0.01	0.85	0.50	0.65	–	1.15
4	0.37	0.40	<0.01	0.77	0.32	0.91	–	1.23
5	0.35	0.42	<0.01	0.77	0.28	0.93	0.01	1.22
6	0.30	0.47	–	0.77	0.26	0.96	0.01	1.23
7	0.26	0.51	–	0.77	0.24	0.99	<0.01	1.23
8	0.30	0.53	–	0.83	0.53	0.65	–	1.18
9	0.31	0.54	–	0.85	0.54	0.61	–	1.15
10	0.28	0.57	<0.01	0.85	0.51	0.60	0.03	1.14
11	0.19	0.61	<0.01	0.80	0.39	0.81	–	1.20
12	0.13	0.65	<0.01	0.78	0.37	0.84	<0.01	1.21
13	0.13	0.67	<0.01	0.80	0.37	0.83	–	1.20
14	0.11	0.68	–	0.79	0.39	0.82	–	1.21
15	0.11	0.69	–	0.80	0.38	0.81	–	1.19
16	0.10	0.70	–	0.80	0.38	0.81	–	1.19

Results of EDS electron-microprobe analyses (listed in order of decreasing content of Ni) of the (Ni,Pd)(Te,Sb,Bi)<sub>1+x</sub> phases enclosed by pyrrhotite, chalcopyrite and magnetite. n.d.: not detected. The total in analysis no. 16 includes 0.39 wt.% As. The atomic proportions are based on two atoms per formula unit (*apfu*).

TABLE 3. COMPOSITION OF SUDBURYITE – (KOTULSKITE) FROM THE WELLGREEN Ni–Cu–PGE DEPOSIT

No.	Pd	Ni	Pt	Sb	Te	Bi	Total	
1 wt%	40.6	3.4	n.d.	49.8	0.58	5.0	99.38	
2	45.0	1.1	n.d.	51.7	0.93	0.97	99.70	
3	40.8	2.9	0.31	48.1	2.3	5.7	100.11	
4	39.4	3.9	0.32	47.8	3.4	5.7	100.52	
5	43.4	1.3	n.d.	48.9	4.2	2.3	100.10	
6	45.0	0.79	n.d.	46.4	5.7	2.1	99.99	
7	29.3	10.9	n.d.	53.4	6.2	n.d.	99.80	
8	44.8	0.59	n.d.	43.8	7.2	3.0	99.39	
9	43.4	1.0	n.d.	43.6	8.9	3.1	100.0	
10	42.5	0.18	n.d.	36.6	10.8	9.9	99.98	
11	44.4	0.70	n.d.	39.2	11.4	4.3	100.0	
12	43.2	1.1	n.d.	43.0	12.7	n.d.	100.0	
13	38.2	3.1	n.d.	37.3	13.5	7.9	100.0	
14	42.0	0.89	n.d.	33.7	16.9	6.5	99.99	
15	42.0	0.43	0.22	23.7	22.2	11.2	99.75	
	Pd	Ni	Pt	ΣMe	Sb	Te	Bi	Σ
1 <i>apfu</i>	0.87	0.13	<0.01	1.00	0.93	0.01	0.05	0.99
2	0.96	0.04	–	1.00	0.97	0.02	0.01	1.00
3	0.88	0.11	–	0.99	0.90	0.04	0.06	1.00
4	0.84	0.15	<0.01	0.99	0.89	0.06	0.06	1.01
5	0.93	0.05	–	0.98	0.92	0.08	0.03	1.03
6	0.97	0.03	–	1.00	0.87	0.10	0.02	0.99
7	0.58	0.39	–	0.97	0.92	0.10	–	1.02
8	0.98	0.02	–	1.00	0.84	0.13	0.03	1.00
9	0.94	0.04	–	0.98	0.83	0.16	0.03	1.02
10	0.96	<0.01	–	0.97	0.72	0.20	0.11	1.03
11	0.97	0.03	–	1.00	0.75	0.21	0.05	1.01
12	0.93	0.04	–	0.97	0.81	0.23	–	1.04
13	0.83	0.12	–	0.95	0.71	0.25	0.09	1.05
14	0.93	0.04	–	0.97	0.65	0.31	0.07	1.03
15	0.96	0.02	<0.01	0.98	0.47	0.42	0.13	1.02

Results of EDS electron-microprobe analyses (listed in order of decreasing content of Sb) of sudburyite grains enclosed by chalcopyrite, pyrrhotite and magnetite. n.d.: not detected. The atomic proportions are based on two atoms per formula unit (*apfu*).

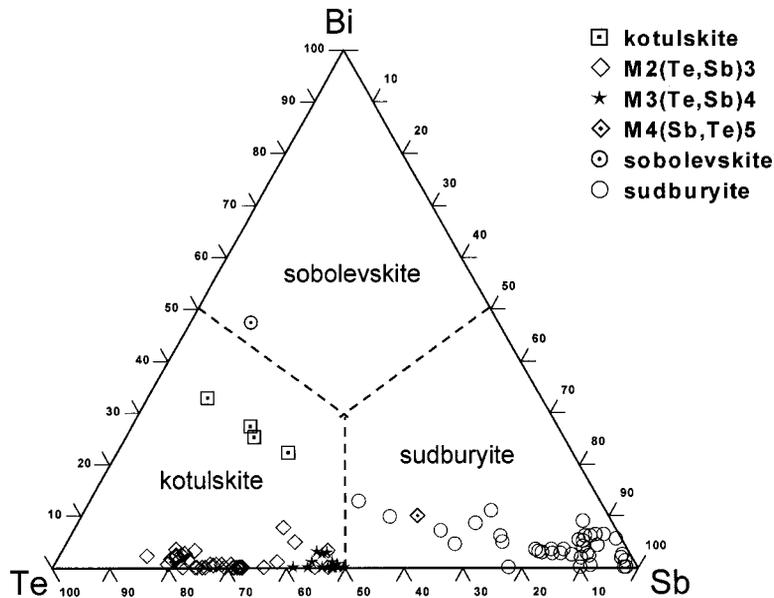


FIG. 3. Compositional variation of the sudburyite–kotulskite–sobolevskite solid solution in the Wellgreen deposit. Results of 43 analyses of sudburyite, kotulskite and sobolevskite and of 59 analyses of phases of the type  $Me(Te,Sb,Bi)_{1+x}$  are projected onto the Te–Bi–Sb ternary (atomic proportions).

bers are close to being stoichiometric  $Me_{1.0}(Sb,Te,Bi)_{1.0}$  (Fig. 4). A strong negative correlation (correlation coefficient  $R = -0.98$ ) is observed between the content of Ni and Pd in this series (Fig. 5). The content of Pd correlates negatively ( $R = -0.92$ ) with the total of semimetals (Fig. 6A). In contrast, the content of Ni correlates positively with this total ( $R = 0.84$ ) (Fig. 6B). The Pd-rich members, which have a lower content of semimetals, are thus more closely stoichiometric in this series, and their atomic ratio (Pd + Pt + Ni) : (Te + Sb + Bi + As) is thus closer to 1 : 1. In contrast, the Ni-rich members are relatively enriched in semimetals (or are metal-deficient), and their compositions more strongly deviate from the 1 : 1 stoichiometry and display the lowest value, 0.57, of the atomic ratio (Pd + Pt + Ni) : (Te + Sb + Bi + As).

Correlations between metals and semimetals in the solid solution of sudburyite, kotulskite, sobolevskite and  $Me(Te,Sb,Bi)_{1+x}$  also are notable. Pd displays a negative correlation with Te ( $R = -0.86$ ) and a positive correlation with Sb ( $R = 0.69$ ) and Bi ( $R = 0.43$ ). In contrast, Ni correlates positively with Te ( $R = 0.78$ ) and negatively with both Sb ( $R = -0.60$ ) and Bi ( $R = -0.45$ ).

#### *Solid solutions of palladoan melonite, merenskyite and moncheite*

Results of electron-microprobe analyses (Tables 6–8, Fig. 7) reveal the presence at Wellgreen of broad

TABLE 6. COMPOSITION OF MELONITE – (MERENSKYITE – MONCHEITE) FROM THE WELLGREEN Ni–Cu–PGE DEPOSIT

No.	Pd	Ni	Pt	Sb	Te	Bi	Total
1 wt.%	3.0	17.5	n.d.	1.6	78.0	n.d.	100.1
2	2.9	17.1	n.d.	n.d.	79.0	1.1	100.1
3	5.1	14.8	1.8	n.d.	75.2	3.2	100.1
4	7.0	14.4	0.42	1.3	74.3	2.6	100.0
5	8.9	13.3	0.29	n.d.	77.5	n.d.	100.0
6	10.9	12.7	n.d.	n.d.	76.4	n.d.	100.0
7	3.4	12.4	9.3	n.d.	74.9	n.d.	100.0
8	11.2	11.0	0.45	n.d.	75.0	2.3	99.95
9	14.2	9.4	n.d.	0.59	73.0	2.2	99.39
10	10.5	8.6	6.9	n.d.	74.0	n.d.	100.0
11*	9.2	5.1	16.8	1.0	60.7	7.2	100.0

	Pd	Ni	Pt	$\Sigma Me$	Sb	Te	Bi	$\Sigma$
1 <i>appfu</i>	0.09	0.94	–	1.03	0.04	1.93	–	1.97
2	0.09	0.93	–	1.02	–	1.97	0.02	1.99
3	0.16	0.83	0.03	1.02	–	1.93	0.05	1.98
4	0.21	0.80	<0.01	1.02	0.03	1.90	0.04	1.97
5	0.27	0.74	<0.01	1.01	–	1.98	–	1.98
6	0.33	0.71	–	1.04	–	1.96	–	1.96
7	0.11	0.72	0.16	0.99	–	2.01	–	2.01
8	0.35	0.63	0.01	0.99	–	1.97	0.04	2.01
9	0.45	0.54	–	0.99	0.02	1.95	0.04	2.01
10	0.34	0.51	0.12	0.97	–	2.02	–	2.02
11*	0.33	0.34	0.33	1.00	0.03	1.83	0.13	1.99

Results of EDS electron-microprobe analyses (listed in order of decreasing content of Ni) of melonite grains enclosed by pyrrhotite and chalcopyrite. \* Intermediate member of the melonite – merenskyite – moncheite series. n.d.: not detected. The atomic proportions are based on three atoms per formula unit (*appfu*).

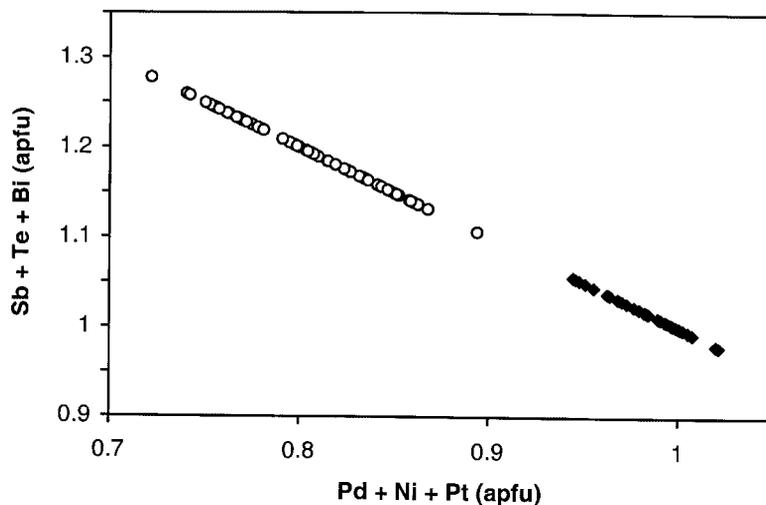


FIG. 4. Plot of the content of semimetals (Sb + Te + Bi) and metals (Pd + Ni + Pt) in atoms per formula unit, *apfu* ( $\Sigma$  atoms = 2) for sudburyite, kotulskite, sobolevskite (filled diamonds) and the phases  $Me(Te,Sb,Bi)_{1+x}$  (open circles) from Wellgreen.

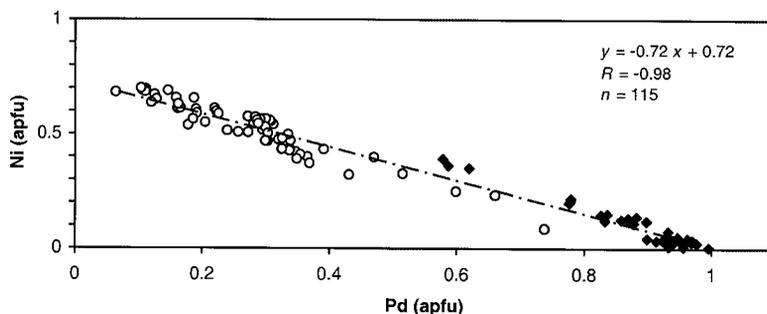


FIG. 5. Ni – Pd correlation (in *apfu*) in the compositions of sudburyite, kotulskite, sobolevskite (filled diamonds) and the phases  $Me(Te,Sb,Bi)_{1+x}$  (open circles) from Wellgreen.

ranges of a solid solution involving melonite, merenskyite and moncheite.

#### *Testibiopalladite–michenerite solid-solution series*

The analytical data reveal the existence at Wellgreen of a solid solution between testibiopalladite and michenerite, which is nearly continuous (Tables 9, 10, Fig. 8A). The correlation between the content of Bi and Sb is strong in this series ( $R = -0.99$ ), and the total content of (Sb + Bi) markedly varies (Fig. 8B). The incorporation of a substantial amount of Ni, 0.13 to 2.8 wt.% (up to 0.18 *apfu* Ni), mean 1.28 wt.% Ni, is noteworthy (Fig. 8C). The highest content of Ni was observed in a grain of testibiopalladite enclosed by pyrrhotite; it con-

tains a high level of Pt: 12.6 wt.% (0.24 *apfu* Pt). The Ni content of the testibiopalladite–michenerite series correlates negatively with Pd ( $R = -0.84$ ), and Pd correlates negatively with Pt ( $R = -0.84$ ). In contrast, the Ni–Pt correlation is weakly positive ( $R = 0.48$ ).

#### *Palladoan imgreite or hexatestibiopanicelkite*

The composition of palladoan imgreite (or hexatestibiopanicelkite) at Wellgreen is: Ni 21.5, Pd 15.9, Pt (and Bi) not detected, Te 32.8, Sb 29.8, total 100.0 wt.%; the formula is  $(Ni_{0.72}Pd_{0.29})_{\Sigma 1.01}(Te_{0.51}Sb_{0.48})_{\Sigma 0.99}$  (basis:  $\Sigma$  atoms = 2) [or  $(Ni_{1.44}Pd_{0.59})_{\Sigma 2.03}Te_{1.01}Sb_{0.96}$ ;  $\Sigma$  atoms = 4)].

## Stibiopalladinite or mertieite II

Owing to the small grain-size, X-ray powder-diffraction data for a Pd-rich antimonide, stibiopalladinite or

mertieite II, could not be obtained. The close similarity of composition observed between these PGM (Cabri & Chen 1976) does not allow us to specify the mineral species on the basis of the composition. The average

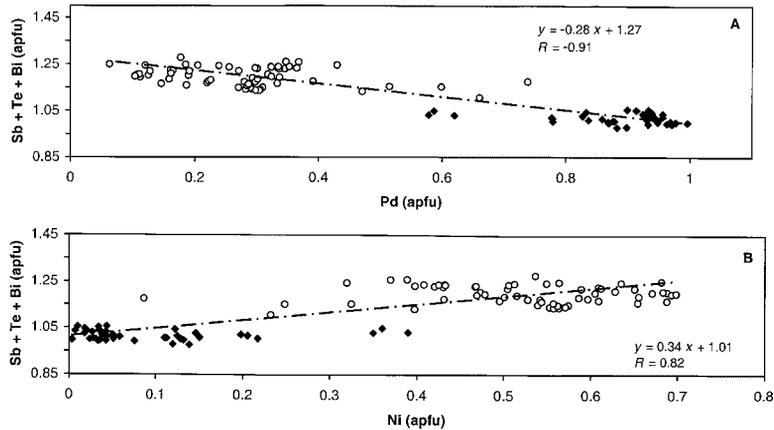


FIG. 6. Plots of content of (Sb + Te + Bi) versus Pd (A) and Ni (B) (in apfu;  $\Sigma$  atoms = 2) for sudburyite, kotulskite, sobolevskite (filled diamonds) and the phases  $Me(Te, Sb, Bi)_{1+x}$  (open circles) from Wellgreen.

TABLE 7. COMPOSITION OF MERENSKYITE - (MELONITE - MONCHEITE) FROM THE WELLGREEN Ni-Cu-PGE DEPOSIT

No.	Pd	Ni	Pt	Sb	Te	Bi	Total
1 wt.%	17.5	8.2	n.d.	0.54	73.8	n.d.	100.0
2	17.2	6.5	0.68	n.d.	61.2	14.4	100.0
3	18.8	5.8	1.8	0.87	66.4	6.4	100.1
4	19.8	5.0	0.16	n.d.	61.1	14.0	100.1
5	11.6	4.2	14.3	n.d.	54.7	15.2	100.0
6	21.7	4.0	0.17	n.d.	60.8	13.4	100.1
7	21.9	3.8	n.d.	0.53	58.6	13.9	98.7
8	11.9	3.2	16.9	n.d.	59.5	8.5	100.0
9	12.8	2.7	15.5	1.0	58.3	9.7	100.0
10	25.1	1.4	0.27	n.d.	54.6	18.6	100.0
11	26.3	0.77	0.14	0.46	62.3	8.9	98.9

	Pd	Ni	Pt	$\Sigma Me$	Sb	Te	Bi	$\Sigma$
1 apfu	0.56	0.47	-	1.03	0.02	1.96	-	1.98
2	0.59	0.40	0.01	1.00	-	1.75	0.25	2.00
3	0.63	0.35	0.03	1.01	0.03	1.85	0.11	1.99
4	0.68	0.31	<0.01	0.99	-	1.76	0.25	2.01
5	0.43	0.28	0.29	1.00	-	1.70	0.29	1.99
6	0.75	0.25	<0.01	1.00	-	1.76	0.24	2.00
7	0.77	0.24	-	1.01	0.02	1.72	0.25	1.99
8	0.44	0.22	0.34	1.00	-	1.84	0.16	2.00
9	0.48	0.18	0.31	0.97	0.03	1.81	0.18	2.02
10	0.91	0.09	<0.01	1.01	-	1.65	0.34	1.99
11	0.93	0.05	<0.01	0.99	0.01	1.84	0.16	2.01

Results of EDS electron-microprobe analyses (listed in order of decreasing content of Ni) of merenskyite grains enclosed by pyrrhotite, chalcopyrite and pyrite. n.d.: not detected. The atomic proportions are based on three atoms per formula unit (apfu).

TABLE 8. COMPOSITION OF MONCHEITE - (MERENSKYITE - MELONITE) FROM THE WELLGREEN Ni-Cu-PGE DEPOSIT

No.	Pd	Ni	Pt	Sb	Te	Bi	Total
1 wt.%	n.d.	0.46	43.5	n.d.	56.0	n.d.	100.0
2	n.d.	0.23	42.3	n.d.	48.9	8.6	100.0
3	1.9	1.5	34.2	n.d.	44.8	17.5	99.9
4	2.3	3.7	29.8	0.89	54.3	9.1	100.1
5	3.9	2.6	28.7	n.d.	56.9	7.9	100.0
6	5.4	2.9	26.2	0.71	56.1	8.7	100.0
7	6.8	3.5	23.3	n.d.	54.7	11.7	100.0
8	8.5	3.4	22.1	0.29	57.8	7.9	100.0
9	7.0	4.1	21.7	n.d.	56.9	10.1	99.8
10	11.0	1.7	20.8	n.d.	54.7	11.7	99.9
11	10.2	3.2	18.9	0.5	59.1	8.2	100.1

	Pd	Ni	Pt	$\Sigma Me$	Sb	Te	Bi	$\Sigma$
1 apfu	-	0.04	1.00	1.04	-	1.97	-	1.97
2	-	0.02	1.01	1.03	-	1.78	0.19	1.97
3	0.08	0.12	0.80	1.00	-	1.61	0.38	1.99
4	0.09	0.26	0.64	0.99	0.03	1.79	0.18	2.00
5	0.15	0.19	0.62	0.96	-	1.88	0.16	2.04
6	0.21	0.21	0.56	0.98	0.02	1.83	0.17	2.02
7	0.26	0.25	0.49	1.00	-	1.77	0.23	2.00
8	0.32	0.23	0.46	1.01	0.01	1.83	0.15	1.99
9	0.27	0.28	0.45	1.00	-	1.80	0.19	1.99
10	0.43	0.12	0.44	0.99	-	1.78	0.23	2.01
11	0.38	0.22	0.39	0.99	0.02	1.84	0.16	2.02

Results of EDS electron-microprobe analyses (listed in order of decreasing content of Pt) of moncheite grains enclosed by pyrrhotite and chalcopyrite. n.d.: not detected. The atomic proportions are based on three atoms per formula unit (apfu).

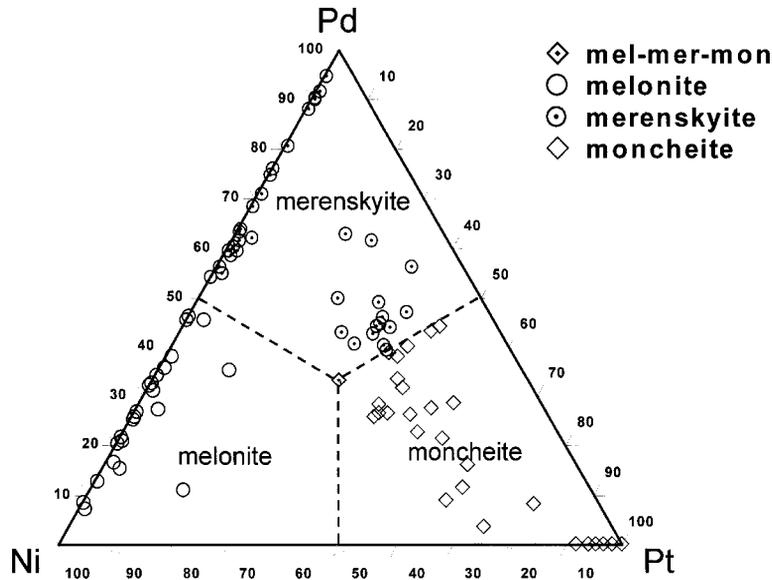


Fig. 7. Compositional variation of solid solution of palladoan melonite, merenskyite and moncheite in the Wellgreen deposit. Results of 93 analyses are projected onto the Ni – Pd – Pt ternary (atomic proportions). A grain with a composition representing 1/3 melonite, 1/3 merenskyite and 1/3 moncheite is shown as mel–mer–mon.

TABLE 9. COMPOSITION OF TESTIBIOPALLADITE – MICHENERITE FROM THE WELLGREEN Ni–Cu–PGE DEPOSIT

No.	Pd	Pt	Ni	Sb	Bi	Te	Total
1 wt.%	27.9	n.d.	1.7	34.1	n.d.	36.3	100.0
2	25.9	0.19	2.3	31.4	1.6	38.6	99.99
3	26.6	0.23	2.2	32.7	2.1	36.1	99.93
4	17.1	12.60	2.8	32.2	3.0	32.2	99.9
5	27.1	n.d.	1.3	28.0	4.6	39.0	100.0
6	26.7	n.d.	1.9	27.4	5.2	38.8	100.0
7	27.7	0.55	0.98	27.7	6.3	36.5	99.73
8	26.2	0.32	1.7	24.6	7.0	39.9	99.72
9	27.1	n.d.	1.6	25.1	7.9	37.9	99.6
10	26.0	0.23	1.6	24.4	8.9	38.5	99.63
11	25.1	1.6	1.7	24.8	10.2	36.6	100.0
12	25.8	n.d.	1.3	18.9	13.5	40.2	99.7
13	27.2	n.d.	0.45	17.3	19.6	35.0	99.55
14	26.4	n.d.	0.56	14.5	23.0	35.2	99.66
15	24.2	n.d.	1.3	13.6	24.3	36.6	100.0
16	25.6	n.d.	0.54	9.7	28.3	34.0	98.14
17	23.3	1.2	1.1	7.8	34.5	32.1	100.0
18	24.0	0.32	0.95	5.6	36.2	32.9	99.97
19	21.0	2.6	1.4	6.9	37.5	30.6	100.0
20	24.1	n.d.	0.43	5.9	38.4	31.2	100.03
21	23.3	1.5	0.13	2.7	42.1	30.2	99.93

Results of EDS electron-microprobe analyses (listed in order of increasing content of Bi) of the testibiopalladite–michenerite enclosed by pyrrhotite, chalcocopyrite and magnetite. n.d.: not detected.

TABLE 10. ATOMIC PROPORTIONS IN TESTIBIOPALLADITE – MICHENERITE FROM FROM THE WELLGREEN Ni–Cu–PGE DEPOSIT

No.	Pd	Pt	Ni	ΣMe	Sb	Bi	Sb+Bi	Te
1 <i>apfu</i>	0.92	–	0.10	1.02	0.98	–	0.98	1.00
2	0.86	<0.01	0.14	1.00	0.91	0.03	0.94	1.07
3	0.88	<0.01	0.13	1.02	0.95	0.04	0.98	1.00
4	0.60	0.24	0.18	1.02	0.99	0.05	1.04	0.94
5	0.92	–	0.08	1.00	0.83	0.08	0.91	1.10
6	0.90	–	0.12	1.02	0.81	0.09	0.90	1.09
7	0.95	0.01	0.06	1.02	0.83	0.11	0.94	1.04
8	0.90	<0.01	0.11	1.01	0.73	0.12	0.85	1.14
9	0.93	–	0.10	1.03	0.75	0.14	0.89	1.08
10	0.90	<0.01	0.10	1.00	0.74	0.16	0.90	1.11
11	0.87	0.03	0.11	1.01	0.75	0.18	0.93	1.06
12	0.91	–	0.08	0.99	0.58	0.24	0.82	1.18
13	0.99	–	0.03	1.02	0.55	0.36	0.91	1.06
14	0.98	–	0.04	1.02	0.47	0.43	0.90	1.09
15	0.89	–	0.09	0.98	0.44	0.46	0.90	1.13
16	0.99	–	0.04	1.03	0.33	0.56	0.89	1.09
17	0.91	0.03	0.08	1.02	0.27	0.68	0.95	1.04
18	0.94	<0.01	0.07	1.01	0.19	0.72	0.91	1.07
19	0.83	0.06	0.10	0.99	0.24	0.76	1.00	1.01
20	0.96	–	0.03	0.99	0.20	0.78	0.98	1.03
21	0.95	0.03	0.01	0.99	0.10	0.88	0.98	1.03

Results of electron-microprobe analyses (in wt.%) are listed in Table 9. The compositions are calculated on the basis of three atoms per formula unit.

result of electron-microprobe analyses of two grains of the antimonide are Pd 70.45, Pt (and Bi) not detected, Ni 0.42, Sb 25.9, As 2.2, Te 0.89, the total is 99.9 wt.%;

such a composition corresponds to the mertieite-II-type formula:  $(Pd_{7.93}Ni_{0.09})_{\Sigma 8.02}(Sb_{2.55}As_{0.35}Te_{0.08})_{\Sigma 2.98}$ . The analysis of the third grain implies that it may well be

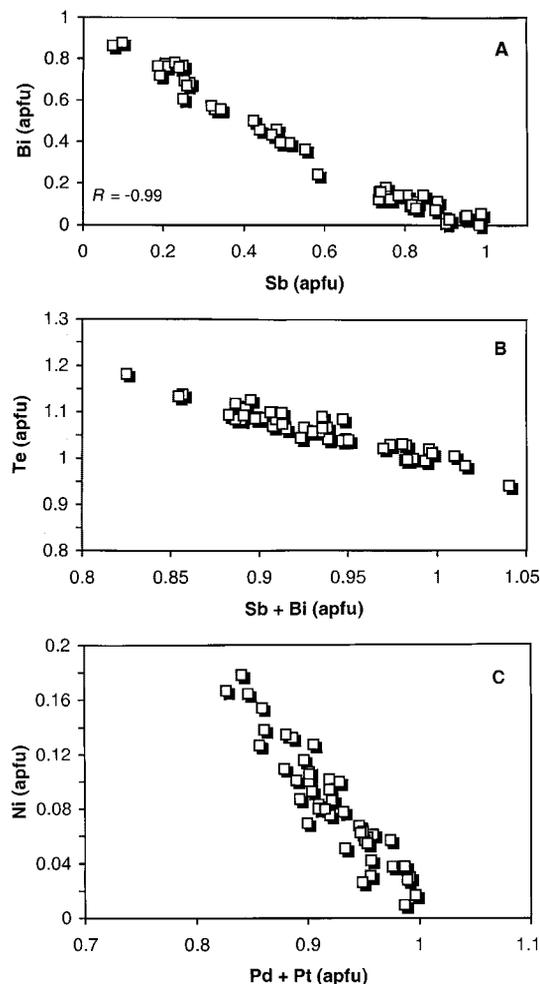


FIG. 8. Concentration of Bi versus Sb (A), Te versus (Sb + Bi) (B) and Ni versus (Pd + Pt) (C) (in apfu;  $\Sigma$  atoms = 3) for the michenerite–testibiopalladite series from Wellgreen. Results of 48 analyses are plotted.

TABLE 11. COMPOSITION OF Pt–Pd–Fe–Cu ALLOYS FROM THE WELLGREEN Ni–Cu–PGE DEPOSIT

No.	Pt	Pd	Fe	Cu	Ni	Total
1 wt. %	75.9	1.1	14.8	6.4	2.3	100.5
2	79.7	5.2	12.7	0.43	2.0	100.0
1 at. %	48.38	1.28	32.95	12.52	4.87	100.0
2	56.30	6.74	31.33	0.94	4.70	100.0

Results of EDS electron-microprobe analyses.

stibiopalladinite: Pd 68.1, Pt 0.38, Sb 29.7, Ni, As and Bi not detected, Te 0.75, the total is 98.9 wt.%; the formula is  $(\text{Pd}_{5.02}\text{Pt}_{0.02})_{\Sigma 5.04}(\text{Sb}_{1.91}\text{Te}_{0.05})_{\Sigma 1.96}$ .

#### Geversite

A representative composition of geversite determined by electron-microprobe analysis, Pt 42.6, Pd not detected, Ni 0.57, Sb 46.6, Bi 7.6, Te 2.4, and As 0.2, for a total of 100.0 wt.%, leads to the formula  $(\text{Pt}_{0.98}\text{Ni}_{0.04})_{\Sigma 1.02}(\text{Sb}_{1.72}\text{Bi}_{0.16}\text{Te}_{0.08}\text{As}_{0.01})_{\Sigma 1.97}$ .

#### Pt–Pd–Fe–(Cu) alloys

The composition suggests that one of the alloy grains is tetraferroplatinum enriched in Cu and Ni (Table 11); the formula is  $(\text{Pt}_{0.97}\text{Pd}_{0.03})_{\Sigma 1.00}(\text{Fe}_{0.66}\text{Cu}_{0.25}\text{Ni}_{0.10})_{\Sigma 1.01}$  (basis:  $\Sigma$  atoms = 2). An alloy of a similar composition, the likely variant of tetraferroplatinum that also contains 0.25 apfu Cu, was previously reported from the Onverwacht deposit, Bushveld complex (Cabri *et al.* 1977). The other grain has the composition  $(\text{Pt}_{2.25}\text{Pd}_{0.27})_{\Sigma 2.52}\text{Fe}_{1.25}\text{Ni}_{0.19}\text{Cu}_{0.04}$  ( $\Sigma$  atoms = 4) (Table 11). It may be native platinum or isoferroplatinum; an unequivocal identification requires X-ray powder-diffraction data (*cf.* Cabri & Feather 1975), which could not be obtained owing to the small grain-size.

#### Pd-rich breithauptite

Breithauptite is an important Pd-bearing phase in the Wellgreen deposit (Cabri *et al.* 1993). Its composition is close to being stoichiometric  $(\text{Ni,Pd})(\text{Sb,As,Te})$ . An elevated level of Pd is invariably observed in the breithauptite (4.1–18.9 wt. % Pd: 0.07–0.35 apfu), along with substantial concentrations of As and Te (Table 12).

#### Trace levels of Pd in ullmannite–(gersdorffite)

Compositions of the ullmannite at Wellgreen are close to ideal  $\text{Ni}(\text{Sb,As})\text{S}$ , and indicate a great extent of the As-for-Sb substitution (Table 13), which is not unusual (*e.g.*, Bayliss 1986). Thirty-five WDS electron-microprobe analyses were carried out, which show that a trace concentration of Pd (up to 0.09 wt.%) is present in solid solution in ullmannite–gersdorffite from sample #2. The minimum detection limit (MDL) for Pd was 0.02 wt.%, and the level of Pt was below the MDL value (0.06 wt.%) in all of these analyses.

#### Trace levels of PGE in base-metal sulfides

The main base-metal sulfides (pentlandite, chalcopyrite and pyrrhotite) were quantitatively analyzed for Pd, Rh and Ru with a proton microprobe; the MDL values are in the range of *ca.* 4 to 7 ppm (Cabri *et al.* 1993). These analyses show that pentlandite is the principal carrier of the PGE among these sulfides. The average

concentrations of the PGE in pentlandite are: Pd 11.4 ppm, Rh 4.0 ppm, and Ru 3.9 ppm. Very few grains of chalcopyrite contain PGE above the MDL values. Three grains of chalcopyrite contain trace Pd (6.4 to 9 ppm), and the two other grains contain Ru and Rh (10 ppm each). As in the case of chalcopyrite, very few grains of pyrrhotite contain the PGE close to MDL values, and only one grain of pyrrhotite contains 5.6 ppm Pd, above the MDL value.

DISCUSSION

*Complex solid-solution involving sudburyite, kotulskite, sobolevskite and (Ni,Pd)(Te,Sb,Bi)<sub>1+x</sub>*

The Pd–(Ni–Pt) antimonotellurides and bismuthotellurides are the most abundant Pd minerals at Wellgreen, as is the case of many other deposits, such as Kambalda, Australia (Hudson 1986) and Donaldson West, Quebec (Dillon-Leitch *et al.* 1986). The significant extent of Ni incorporation in various PGM is a prominent feature at Wellgreen.

The extent of mutual solid-solution of PdSb, PdTe and PdBi in the Wellgreen deposit (Tables 3, 4, Fig. 3) is greater than that documented at Sudbury, the type locality for sudburyite (Cabri & Laflamme 1974, 1976), at Kambalda (Hudson & Donaldson 1984), and at Blue Lake (Beaudoin *et al.* 1990). A general decrease in temperature may have favored the Te-for-Sb substitution along the sudburyite–kotulskite binary join (up to 41 mol.% PdTe, Table 3), consistent with a higher melting point of synthetic sudburyite (800°C) than of kotulskite (750°C; Kim 1987).

Phases of the type *Me*<sub>1.00</sub>(Te,Sb,Bi)<sub>1+x</sub> (Fig. 4) seem to be related with the sudburyite – kotulskite –

(sobolevskite) solid-solution series. These phases display an excess in the content of semimetals relative to the 1 : 1 stoichiometry, and thus have low values of the atomic ratio (Pd + Pt + Ni) : (Te + Sb + Bi + As), 0.81 to 0.57. A strong negative Ni–Pd correlation (*R* = –0.98) and gradual variations and continuous trends of composition are observed at Wellgreen (Figs. 4–6). These characteristics argue for the existence of a complex solid-solution, which involves, as end-members, sudburyite – kotulskite – (sobolevskite) and (Ni,Pd)(Te,Sb,Bi)<sub>1+x</sub> [or (Ni,Pd)<sub>1-x</sub>(Te,Sb,Bi)]. The member of the series richest in Ni displays a strong predominance of Ni over Pd: (Ni<sub>0.87</sub>Pd<sub>0.13</sub>)(Te<sub>1.00</sub>Sb<sub>0.47</sub>As<sub>0.01</sub>)<sub>Σ1.48</sub> (basis: Σ metals = 1) [or (Ni<sub>0.58</sub>Pd<sub>0.09</sub>)<sub>Σ0.67</sub>(Te<sub>0.67</sub>Sb<sub>0.32</sub>); basis: Σ semimetals = 1]. The extent of nonstoichiometry (*i.e.*, deviation from the 1 : 1 stoichiometry) of this solid-solution series is a function of the content of Ni and Pd, so that the members richest in Pd are closest to the 1 : 1 stoichiometry. The total content of semimetals increases with an increase in Ni. In contrast, an increase in Pd is accompanied by a decrease in the total content of semimetals (Fig. 6).

Thus, the compositions observed at Wellgreen imply that the complex solid-solution extends from sudburyite – kotulskite – (sobolevskite) to the phase (Ni,Pd)(Te,Sb,Bi)<sub>1.5</sub>, which is intermediate in composition between palladoan imgreite [(Ni,Pd)(Te,Sb)] and palladoan melonite [(Ni,Pd)(Te,Sb)<sub>2</sub>]. A structural simi-

TABLE 13. COMPOSITION OF ULLMANNITE–GERSDORFFITE FROM THE WELLGREEN Ni–Cu–PGE DEPOSIT

No.	Ni	Co	Fe	Pd	Sb	As	S	Total
1 wt.%	27.7	0.40	0.07	n.d.	54.9	2.1	14.8	100.0
2	27.7	0.16	0.20	0.07	54.5	2.4	15.1	100.1
3	28.6	0.09	0.07	n.d.	52.7	3.8	15.2	100.5
4	27.5	0.25	0.29	0.03	53.4	3.9	15.0	100.4
5	28.6	0.03	0.03	n.d.	51.8	5.0	15.2	100.7
6	28.35	0.10	0.16	n.d.	51.0	5.4	15.3	100.3
7	28.5	n.d.	0.16	n.d.	50.4	6.2	15.5	100.8
8	28.5	n.d.	0.34	n.d.	49.1	6.6	15.4	99.9
9	28.9	n.d.	0.12	n.d.	48.0	7.3	15.7	100.0
10	29.1	n.d.	0.06	n.d.	47.0	8.5	15.7	100.4

TABLE 12. COMPOSITION OF Pd-RICH BREITHAUPTITE FROM THE WELLGREEN Ni–Cu–PGE DEPOSIT

No.	Ni	Pd	Pt	Co	Fe	Sb	As	Te	S	Total
1 wt.%	30.1	4.6	n.d.	0.28	0.24	61.8	1.9	0.2	n.d.	99.12
2	30.1	4.1	n.d.	n.d.	n.d.	62.3	2.1	0.13	n.d.	98.73
3	29.7	4.8	n.d.	n.d.	0.39	62.6	1.2	0.49	0.17	99.35
4	29.8	4.5	n.d.	n.d.	n.d.	63.6	1.8	1.8	n.d.	101.5
5	29.9	4.5	n.d.	0.07	0.16	62.6	1.8	0.66	0.04	99.73
6 <sup>§</sup>	18.2	18.9	0.19	n.d.	n.d.	60.0	n.d.	2.8	n.d.	100.09

	Ni	Pd	Pt	Co	Fe	ΣMe	Sb	As	Te	S	Σ
1 <i>apfu</i>	0.93	0.08	–	0.01	<0.01	1.02	0.92	0.05	<0.01	–	0.98
2	0.94	0.07	–	–	1.01	0.94	0.05	<0.01	–	–	0.99
3	0.92	0.08	–	–	0.01	1.01	0.94	0.03	<0.01	0.01	0.99
4	0.91	0.08	–	–	–	0.99	0.94	0.04	0.03	–	1.01
5	0.93	0.08	–	<0.01	<0.01	1.02	0.93	0.04	0.01	<0.01	0.98
6	0.62	0.35	<0.01	–	–	0.98	0.98	–	0.04	–	1.02

1–5: Results of WDS electron-microprobe analyses. 6: EDS electron-microprobe analysis. n.d.: not detected. The minimum detection limits are 0.03 wt.% Co and Fe, 0.06 wt.% Pt, 0.08 wt.% As and 0.05 wt.% S. <sup>§</sup> Reported by Cabri *et al.* (1993). The atomic proportions are based on two atoms per formula unit (*apfu*).

	Ni	Co	Fe	Pd	ΣMe	Sb	As	Sb+As	S
1 <i>apfu</i>	1.00	0.01	<0.01	–	1.01	0.95	0.06	1.01	0.98
2	0.99	<0.01	0.01	<0.01	1.00	0.94	0.07	1.01	0.99
3	1.01	<0.01	<0.01	–	1.01	0.90	0.11	1.01	0.98
4	0.98	0.01	0.01	<0.01	1.00	0.91	0.11	1.02	0.98
5	1.00	<0.01	<0.01	–	1.00	0.88	0.14	1.02	0.98
6	1.00	<0.01	0.01	–	1.01	0.86	0.15	1.01	0.98
7	0.99	–	0.01	–	1.00	0.84	0.17	1.01	0.99
8	1.00	–	0.01	–	1.01	0.83	0.18	1.01	0.99
9	1.00	–	<0.01	–	1.00	0.80	0.20	1.00	1.00
10	1.00	–	<0.01	–	1.00	0.78	0.23	1.01	0.99

Results of WDS electron-microprobe analyses (listed in order of increasing content of As), obtained with a JEOL-733 microprobe (counting times: 100 s). Pt was sought, but not detected. The minimum limits of detection are 0.03 wt.% Co, 0.02 wt.% Pd and 0.06 wt.% Pt. The atomic proportions are based on three atoms per formula unit (*apfu*).

larity likely exists among these chalcogenides and favors the formation of such solid solution. Sudburyite, kotulskite and imgreite are considered isostructural, crystallize with the NiAs-type structure, and belong to the nickeline group. Sobolevskite, Pd(Bi,Te), is also considered to be a member of this group (Evshtigeeva *et al.* 1975), though samples of sobolevskite from the type occurrence at Noril'sk may contain an admixture of a monoclinic polymorph of PdBi (Bhatt & Schubert 1979), as was suggested by Bayliss (1990).

#### *The NiTe<sub>1+x</sub> solid solution and related minerals*

The (Ni,Pd)(Te,Sb)<sub>1+x</sub>-type phases from Wellgreen appear to be related to a synthetic solid-solution reported by Carbonara & Hoch (1972). This solid solution, Ni<sub>1-x</sub>Te or NiTe<sub>1+x</sub>, extends from stoichiometric NiTe, having a NiAs-type structure, to NiTe<sub>2</sub> (or Ni<sub>0.5</sub>Te) with the CdI<sub>2</sub>-type structure; the phase field between these end members is reported to be continuous, and the transition occurs close to the composition Ni<sub>0.75</sub>Te (or NiTe<sub>1.33</sub>). The composition of the member richest in Ni (Figs. 5, 6B) in the series observed at Wellgreen is close to (Ni,Pd)(Te,Sb,Bi)<sub>1.5</sub>.

Two Ni-(Te)-rich minerals, namely imgreite, NiTe<sub>1+x</sub> (Yushko-Zakharova 1964) and hexatestibiopanickelite (Chao & Cabri 1976), the revised formula of which is (Ni,Pd)(Te,Sb) (Bayliss 1990), have similar unit-cell parameters and the same space group (*P6<sub>3</sub>/mmc*). These tellurides are structurally related to the nickeline-type solid-solution NiTe<sub>1+x</sub> of Carbonara & Hoch (1972). Yushko-Zakharova (1964) synthesized some members of the imgreite – melonite series. In fact, hexatestibiopanickelite (Ni<sub>0.68</sub>Pd<sub>0.30</sub>)<sub>Σ0.98</sub>(Te<sub>0.51</sub>Sb<sub>0.51</sub>Bi<sub><0.01</sub>)<sub>Σ1.02</sub> may well be a Pd–Sb-rich member of the imgreite – sudburyite – (breithauptite) series. The incorporation of significant Sb in this sample is not inconsistent, as the Sb-for-Te substitution is quite common in various nickeline-type solid solutions and may be unlimited (*e.g.*, Makovetskii & Shakhlevich 1982, Kim 1987).

#### *Structural formulae of the Pd–Ni ditellurides and monotellurides*

Ditellurides of Pd and transition elements were reported to have the layered CdI<sub>2</sub>-type structure, which is consistent with generalized structural formula  $Me^{4+}(Te^{2-})_2$  (*e.g.*, Pell *et al.* 1996). Within the framework of this model, synthetic PdTe<sub>2</sub> (merenskyite) has a layered structure that involves octahedrally coordinated Pd<sup>4+</sup>. In contrast, Jobic *et al.* (1991) argued that the formula  $Me^{4+}(Te^{2-})_2$  does not adequately characterize the bonding in the transition-metal and related ditellurides, the structure of which is not layered; it was classified by these authors as of “polymeric CdI<sub>2</sub>-type”. Bensch *et al.* (1996) provided further evidence that synthetic NiTe<sub>2</sub> (melonite) does not have a layered structure and

suggested the revised formula Ni<sup>2+</sup>Te<sup>1-</sup><sub>2</sub> instead of the previous formula Ni<sup>4+</sup>(Te<sup>2-</sup>)<sub>2</sub>. By analogy with the revised formula, cations of Pd appear also to be divalent in merenskyite, which is isostructural with melonite, and the likely structural formula of merenskyite thus is Pd<sup>2+</sup>(Te<sub>2</sub>)<sup>2-</sup>. Correspondingly, Ni and Pd appear to be divalent in members of the melonite–merenskyite solid solution.

Tellurium occurs as Te<sup>4+</sup> in sulfosalt minerals (*e.g.*, Trudu & Knittel 1998). In contrast, in various tellurides, Te has a negative oxidation state and exists as Te<sup>2-</sup> ions, (Te<sub>2</sub>)<sup>2-</sup> dumbbells, or both (*e.g.*, Peters *et al.* 1996, Bensch *et al.* 1996, Durand *et al.* 1998). In addition, Te may display an intermediate formal charge, as in synthetic Ir<sup>3+</sup>(Te<sup>1.5-</sup>)<sub>2</sub> (Jobic *et al.* 1991).

The likely structural formula of end-member imgreite is Ni<sup>2+</sup>Te<sup>2-</sup>. Thus, in order to maintain charge balance, an increase in the content of Te in members of the palladoan imgreite – palladoan melonite series may accompany the formation of (Te<sub>2</sub>)<sup>2-</sup> dumbbells at the expense of the Te<sup>2-</sup> ions in the structure(s). This mechanism may also be significant in the solid solution of sudburyite, kotulskite, sobolevskite and palladoan imgreite – palladoan melonite [(Ni,Pd)(Te,Sb,Bi)<sub>1+x</sub>] at Wellgreen.

#### *Occurrences of the phases Me<sub>1.0</sub>(Te,Bi,Sb)<sub>1+x</sub> in other PGE deposits*

Various phases reported in the literature display values of the atomic ratio  $\Sigma \text{metals} : \Sigma \text{semimetals}$  close to 1 : 1, and show a varying excess in the content of semimetals. Such examples include Pd<sub>7</sub>(Te,Bi)<sub>8</sub> from the Konttijärvi intrusion, Finland (Vuorelainen *et al.* 1982), Pd<sub>3</sub>(Te<sub>2</sub>Sb)<sub>2</sub> from the Donaldson West deposit, Quebec (Dillon-Leitch *et al.* 1986), and (Pd,Ni)<sub>0.44</sub>(Te,Sb)<sub>0.56</sub> from the Thompson mine, Manitoba (Chen *et al.* 1993). The value of the  $\Sigma \text{metals} : \Sigma \text{semimetals}$  ratio of the phase from Manitoba is very close to that of the kotulskite-type Pd<sub>45.0</sub>Te<sub>55.0</sub> phase obtained by synthesis (Kim 1987).

Yushko-Zakharova *et al.* (1986) noted that a deficit in Pd, corresponding to an excess in Bi(+Te), is quite common in samples of natural and synthetic kotulskite-type tellurides. To explain this feature, these authors suggested the possibility of a partial Bi-for-Pd substitution. It appears more likely, however, that these “Pd-deficient” phases are in fact members of the kotulskite [ideally Pd<sup>2+</sup>Te<sup>2-</sup>] – merenskyite [Pd<sup>2+</sup>(Te<sub>2</sub>)<sup>2-</sup>] solid-solution series, and they have the generalized formula of Pd(Te,Bi)<sub>1+x</sub>. In this series, (Te<sub>2</sub>)<sup>2-</sup> dumbbells may form at the expense of Te<sup>2-</sup> ions in order to maintain charge balance, as may also be the case for the related imgreite–melonite series. This suggestion is consistent with the two forms of tellurium, Te<sup>2-</sup> ions and (Te<sub>2</sub>)<sup>2-</sup> dumbbells, present in the structure of synthetic Ag<sub>5-x</sub>Te<sub>3</sub> (Peters *et al.* 1996).

Experimental results also are consistent with the suggestion of a continuous solid-solution between synthetic PdTe and PdTe<sub>2</sub> (kotulskite and merenskyite) that was observed at 575–710°C (Hoffman & MacLean 1976, Kim & Chao 1991). The related  $Me_{1.0}(\text{Te,Bi,Sb})_{1+x}$  phases, reported in the literature, also may represent intermediate members of the monochalcogenide (nickeline-type)–dichalcogenide (melonite-type) solid-solution series.

#### *The breithauptite–sudburyite solid solution*

Substantial amounts of the PGE can enter some non-platinum-group minerals of the nickeline group: breithauptite (Nixon *et al.* 1990, Ponomarenko & Malov 1991, Cabri *et al.* 1993) and nickeline (*e.g.*, Watkinson & Ohnenstetter 1992). Several PGM (sudburyite, sobolevskite, niggliite, and stimpflite) also are members of this group, and nickeline-type structures thus clearly favor the incorporation of the PGE.

Breithauptite at Wellgreen typically contains from 4.1 to 4.8 wt.% Pd (0.07–0.08 *apfu*; Table 12). The highest content of Pd was documented in a grain of breithauptite from Wellgreen, which contains 8.9 wt.% Pd (0.35 *apfu*), indicating substitution of *ca.* 36 mol.% sudburyite for breithauptite (Cabri *et al.* 1993). A lower content (0.05 *apfu* Pd) was reported in breithauptite from the Noril'sk complex (Ponomarenko & Malov 1991).

#### *Solid solutions of palladoan melonite, merenskyite and moncheite*

The existence of continuous solid-solutions between merenskyite and melonite, and between merenskyite and moncheite, is well documented in the literature (*e.g.*, Cabri & Laflamme 1981, Garuti & Rinaldi 1986, Hudson 1986, Harney & Merkle 1990). At Wellgreen, there are, in general, two extensive fields of solid solution in the system NiTe<sub>2</sub>–PdTe<sub>2</sub>–PtTe<sub>2</sub> (Fig. 7). The first field is narrow and generally extends along the NiTe<sub>2</sub>–PdTe<sub>2</sub> join. This field involves members of the melonite–merenskyite series, which are quite poor in the end-member moncheite (mainly <10 mol.% PtTe<sub>2</sub>). The second field is broader (Fig. 7), and consists of members of the merenskyite–moncheite series, which are relatively enriched in melonite (10 to 30 mol.% NiTe<sub>2</sub>). Interestingly, a member having an intermediate composition (*i.e.*, 1/3 melonite, 1/3 merenskyite and 1/3 moncheite) was observed at Wellgreen (Fig. 7).

#### *The testibiopalladite–michenerite series*

The solid-solution series between testibiopalladite and michenerite is nearly continuous in the Wellgreen deposit (Fig. 8A). Extensive solid-solution in this series was previously reported from Kambalda (Hudson *et al.*

1978, Hudson 1986) and the Thompson mine, Manitoba (Chen *et al.* 1993).

The existence of two different mechanisms of substitution involving the semimetals is consistent with our analytical results. (1) The Sb-for-Bi substitution is most common in michenerite–testibiopalladite, and is indicated by the strong negative correlation between Sb and Bi ( $R = -0.99$ ; Fig. 8A). (2) The variation in (Sb + Bi), shown in Figure 8B, suggests the existence of the Te-for-(Sb+Bi) substitution in the testibiopalladite–michenerite series.

The extent of incorporation of Ni (and Pt) in the testibiopalladite–michenerite series at Wellgreen also may be quite significant (Fig. 8C). The presence of negative correlations between Pd and Ni, and between Pd and Pt ( $R = -0.84$  each), and a weak positive Ni–Pt correlation ( $R = 0.48$ ) implies that Ni and Pt replace Pd *via* a coupled substitution.

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