

A LASER-RAMAN MICROPROBE STUDY OF PLATINUM-GROUP MINERALS FROM THE MUNNI MUNNI LAYERED INTRUSION, WEST PILBARA BLOCK, WESTERN AUSTRALIA

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ABSTRACT

The laser-Raman microprobe has been used to identify relatively small ($\leq 10 \mu\text{m}$) grains of platinum-group minerals (PGM) occurring in the mineralized layer just below the contact between the ultramafic zone and the gabbroic zone of the Archean Munni Munni layered igneous complex, in the west Pilbara block of Western Australia. The Raman spectra of sperrylite, platarsite, moncheite, cooperite, braggite and potarite are reported for the first time, and their spectra are compared with those predicted from group theory. All Raman bands occur below 500 cm^{-1} , and each PGM produces a distinct spectrum, thus allowing ready identification of each mineral by Raman microspectroscopy. The technique requires little preparation of the samples and offers the advantages of high spatial resolution and the relatively rapid identification of *in situ* micrometer-sized grains of PGM in silicate or sulfide matrices.

Keywords: Raman spectroscopy, laser microprobe, platinum-group minerals, mafic-ultramafic layered intrusion.

SOMMAIRE

Nous avons utilisé une microsonde laser-Raman pour identifier les particules de taille micrométrique ($\leq 10 \mu\text{m}$) de minéraux du groupe du platine dans le niveau minéralisé immédiatement en-dessous du contact entre les zones gabbroïque et ultramafique du massif stratiforme de Munni Munni, dans l'ouest du socle archéen de Pilbara, en Australie occidentale. Les spectres Raman de sperrylite, platarsite, moncheïte, cooperite, braggite et potarite sont ici présentés pour la première fois; ces spectres sont comparés à ceux que l'on prédit à partir de la théorie de groupe. Toutes les bandes du spectre sont situées à moins de 500 cm^{-1} , et chacun de ces minéraux produit un spectre distinct, permettant ainsi une identification facile par micro-spectroscopie Raman. La technique requiert peu d'effort pour préparer les échantillons, et offre comme avantages principaux une résolution spatiale élevée et une identification relativement rapide *in situ* de particules micrométriques des minéraux du groupe du platine inclus dans une matrice silicatée ou sulfurée.

(Traduit par la Rédaction)

Mots-clés: spectroscopie de Raman, microsonde laser, minéraux du groupe du platine, complexe stratiforme mafique-ultramafique.

INTRODUCTION

Raman spectroscopy is a nondestructive, structurally sensitive technique that can be used for the identification of minerals and the characterization of glassy materials (Griffith 1987). The theory and applications of Raman and infrared spectroscopy to mineral studies have recently been summarized by McMillan (1985). Although a complete analysis of the Raman spectrum would require knowledge of the phonon dispersion-curve for each platinum-group mineral (PGM), the expected number of bands in the Raman spectrum can be calculated using the method of factor-group analysis (*cf.* DeAngelis *et al.* 1972). This type of symmetry analysis, in conjunction with the observed Raman and infrared spectra, can provide detailed information on the crystal structure of minerals. It has been

over twenty years since Raman spectroscopy was first applied to the study of sulfide minerals (Ushioda 1972), but no previous Raman studies of natural PGM have been carried out owing to the typically small grain-size of these minerals in most deposits (*e.g.*, usually $\leq 10 \mu\text{m}$ in diameter in the Munni Munni Complex).

Where the PGM grains are only a few micrometers in size, the electron microprobe generally provides only semiquantitative data owing to possible problems with interference from surrounding sulfides. Similarly, analysis by other structurally sensitive techniques, such as X-ray diffraction (XRD) and transmission electron microscopy (TEM), are quite difficult owing to problems with mineral separation and sample manipulation. Use of the proton microprobe for the analysis of sulfide minerals is now widely accepted (*e.g.* Cabri *et al.* 1984,

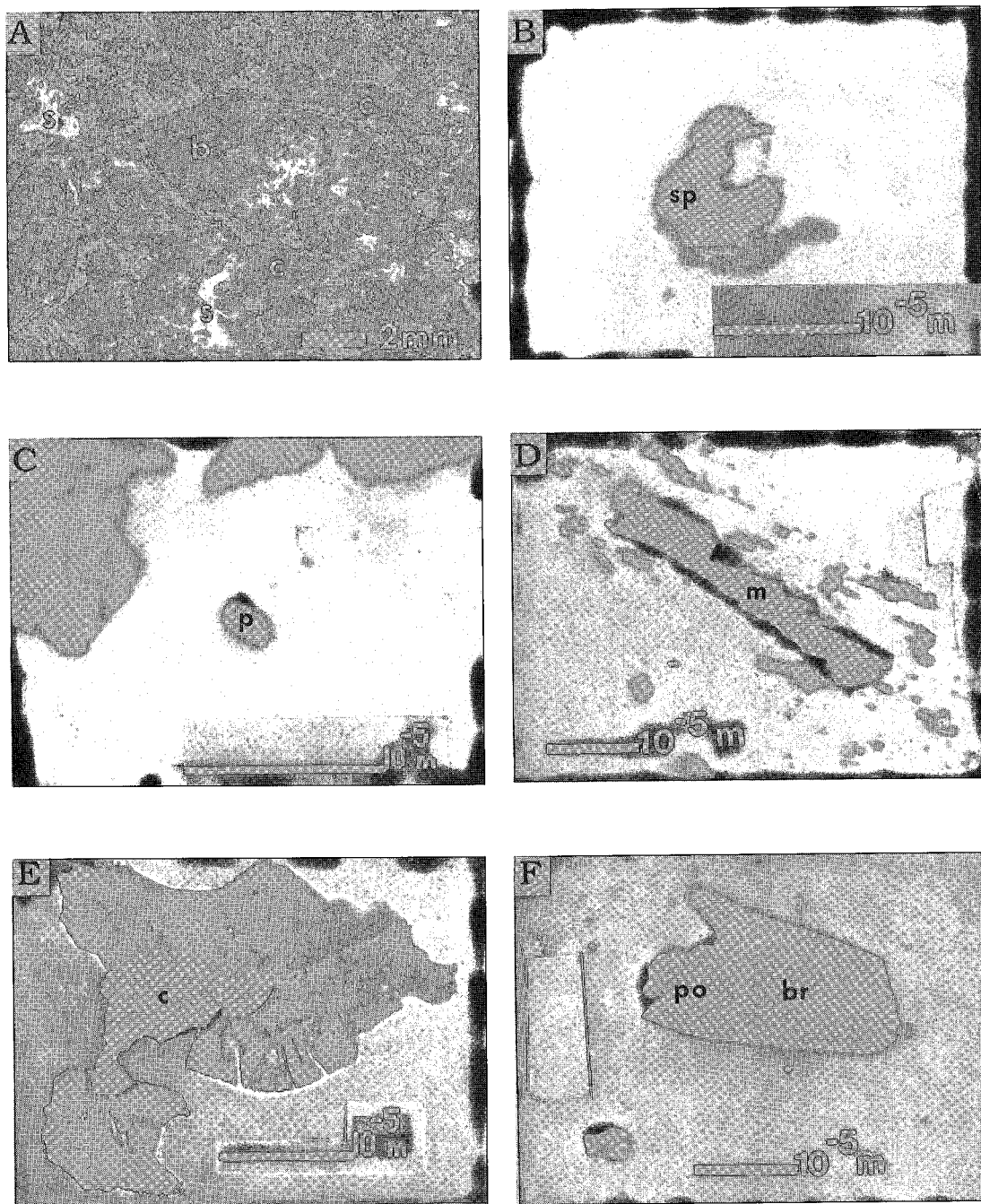


FIG. 1. Photomicrographs of PGM grains (plane-polarized light) from the upper levels of the porphyritic websterite orthocumulate layer of the Munni Munni Complex. A. Large euhedral grain of enstatite (b) and smaller cumulus clinopyroxene (c) with intercumulus plagioclase (p) and local chalcopyrite – pentlandite – pyrrhotite sulfide blebs (s). B. Sperrylite (sp) with chalcopyrite. C. Platarsite (p) in a silicate matrix. D. Grains of moncheite (m) subaligned with small stringers of chalcopyrite. E. Cooperite (c) in contact with a chalcopyrite – pentlandite aggregate. F. Potarite (po) in contact with a large crystal of braggite (br).

1985, Cabri 1988), and it has recently been applied to the analysis of PGM (Tamana *et al.* 1994). However, the size of the beam (typically $>10\text{ }\mu\text{m}$) and the greater depth of penetration of the protons can lead to interference and matrix effects in the case of small grains (Cabri *et al.* 1984, Czamanske *et al.* 1992).

The laser-Raman microprobe has a spatial resolution of approximately $1\text{ }\mu\text{m}$ and usually does not require any special technique of sample preparation. It has proved to be a convenient, reliable and relatively rapid technique for the identification of micrometric minerals in normal thin sections (Boyer & Smith 1984, Mao *et al.* 1987) and has also been used for the identification of a large number of sulfide minerals in hand specimens, polished blocks and thin sections (Mernagh & Trudu 1993). Hoatson & England (1986) used a scanning electron microscope (SEM) and energy-dispersion techniques to semiquantitatively analyze *in situ* grains of PGM from polished blocks cut from the porphyritic websterite layer at the ultramafic zone – gabbroic zone contact of the Munni Munni Complex.

The geology and mineralization features of the Munni Munni Complex have been described by Donaldson (1974), Hoatson & England (1986), Hoatson & Keays (1989), Williams *et al.* (1990), Hoatson (1991), Barnes *et al.* (1990, 1992), Hoatson *et al.* (1992), and Barnes & Hoatson (1994). Briefly, the Munni Munni Complex covers an area of 9 by 25 km and shows strong similarities in geometry, stratigraphic sequence, and mineralization to the Great Dyke of Zimbabwe (Wilson & Prendergast 1989). The PGE mineralization is associated with disseminated sulfides (mainly chalcopyrite, pyrrhotite, and pentlandite) in the upper levels of a porphyritic websterite orthocumulate layer (Fig. 1A) immediately below the contact between the ultramafic and the gabbroic zones.

In this study, Raman spectra were recorded from the same specimens as used in the study of Hoatson & England (1986) in order to investigate the ease of identification of the PGM by Raman microprobe spectroscopy as compared to the more conventional

TABLE 1. PLATINUM-GROUP MINERALS IN THE MUNNI MUNNI COMPLEX

Major components	Number of grains	Percentage of grains examined	Probable minerals	Ideal formula	Size range (μm)	Mean size (μm)	Associations
Platinum-dominant minerals							
Pt	4	5	Native Pt	Pt	2-6	4	100% Silicates
Pt-Fe	2	2	?Isoferroplatinum	Pt ₂ Fe	2-6	4	100% Silicates
Pt-S	2	2	Cooperite	PtS	12-15	14	50% Silicates, 50% Pn/Ccp
Pt-Pd-S	3	3	Braggite	(Pt,Pd,Ni)S	4-8	6	67% Silicates, 33% Pn
Pt-As	17	19	Sperryllite	PtAs ₂	2-20	5	70% Silicates, 20% Ccp, 10% Pn
Pt-As-S-Fe	7	8	Platarsite	Pt(As,S) ₂	2-10	5	100% Silicates
Pt-As-S-Ru	1	1	?Platarsite	Pt(As,S) ₂	20	20	100% Ccp
Pt-Te	8	9	Moncheite	PtTe ₂	2-30	8	100% Silicates
Pt-Te-As-S	1	1	?Moncheite	PtTe ₂	4	4	100% Silicates
Palladium-dominant minerals							
Pd	4	5	Native Pd	Pd	4-8	6	100% Silicates
Pd-Pt-S	2	2	Braggite	(Pt,Pd,Ni)S	2-25	12	100% Silicates
Pd-Pt-As-Te	2	2	?		4-10	7	100% Silicates
Pd-S-As-Fe	3	3	Vysotskite	(Pd,Pt,Ni)S	2	2	100% Ccp
Pd-S-Te-Fe	3	4	?		2	2	67% Silicates, 33% Py
Pd-Te	13	15	Telluropalladinite	Pd ₅ Te ₄	2-12	5	80% Silicates, 10% Silicates/Ccp, 10% Ccp
Pd-Te-Bi	3	4	Michenerite	PdBiTe	2-8	5	100% Silicates/Ccp
Pd-Hg-As	10	12	Athencite	(Pd,Hg) ₃ As	2-5	4	100% Silicates
			Potarite	PdHg			
Pd-Hg-Te-Cu	2	2	Temagamite	Pd ₃ HgTe ₃	2	2	100% Ccp
Au-dominant mineral							
Au-Ag	1	1	Argentian gold	(Au,Ag)	8	8	100% Silicates

Overall association: Silicates—69 occurrences (78% abundance), Ccp—10 (12%), Pn—3 (3%), Py—1 (1%), Silicates/Ccp—4 (5%), Pn/Ccp—1 (1%). Ccp = chalcopyrite, Pn = Pentlandite, Py = pyrite, Silicates/Ccp = along boundaries of silicates and chalcopyrite.

Note: in some cases for the smaller ($2\text{ }\mu\text{m}$) grains described above, the Cu, Ni, and Fe component may be partly attributed to surrounding Cu-Ni sulphide phases and not the platinum-group mineral. (Adapted from Hoatson & Keays 1989)

technique of electron-microprobe analysis. To our knowledge, these are the first Raman spectra of PGM reported in the literature.

DESCRIPTION AND OCCURRENCE OF PGM

Eighty-seven semiquantitative analyses of the PGM (Table 1) were carried out in the SEM study (Hoatson & England 1986, Hoatson & Keays 1989). Platinum- and palladium-bearing minerals were identified, but minerals containing Rh and Ru were found to be rare. Grains of platinum-dominant minerals ($n = 45$) and palladium-dominant minerals ($n = 42$) are of similar abundance and comprise arsenides, sulfarsenides, tellurides, mercury-bearing arsenides and native metals. Sperrylite (19% of the grains) is the most common, followed by telluropalladinite (15%), potarite or atheneite (12%), moncheite (9%), platarsite (8%), native Pt (5%), and native Pd (5%). Minerals of minor (< 4%) significance include cooperite, braggite, michenerite or kotulskite, temagamite, isoferroplatinum, a Pd-Pt-Sb-Te antimonide and various sulfarsenides of Pd. Platinum- and Pd-bearing sulfides (cooperite, braggite, vysotskite, *etc.*) form a subordinate group (10%) relative to the As-, Te-, Hg-bearing PGM. All PGM encountered have been documented previously from other major mafic-ultramafic intrusions, including the Bushveld, Stillwater, Lac des Iles, Sudbury, New Rambler, and Noril'sk-Talnakh complexes. Potarite is a rarer phase, originally reported from the Potaro River region, Guyana by Harrison (1924); it has been described as a very poorly characterized mineral by Cabri & Laflamme (1981).

Except for the Pt-Pd sulfarsenide minerals, all PGM are $\leq 10 \mu\text{m}$ in average grain-size. The Pt-dominant minerals are marginally coarser-grained (average grain-size $6.5 \mu\text{m}$) than the Pd-bearing phases ($5.0 \mu\text{m}$). The largest grains of PGM (maximum size $30 \times 5 \mu\text{m}$) are enclosed in, or at the boundary of, silicate grains, whereas grains of PGM in Fe-Cu-Ni sulfides are generally smaller. There is a strong spatial association of the PGM with silicate phases. Seventy-eight per cent of the grains of PGM are either totally enclosed within or along grain boundaries of silicate minerals, 12% are within chalcopyrite, 3% within pentlandite, 1% within pyrite, and 6% along grain boundaries between pentlandite and chalcopyrite or between silicate and chalcopyrite. Although the PGM are largely hosted by silicates on a micrometer scale, most are actually spatially associated with sulfides in either of two ways. Firstly, PGM are associated with hydrous silicate assemblages (*e.g.*, actinolite - tremolite - biotite) that appear to result from the *in situ* replacement of Fe-Cu-Ni sulfide blebs. Secondly, PGM that show no direct relationship to pre-existing sulfides still display an association with sulfides, either by parallel alignment with the sulfide grain, or by location near sulfides along cleavage traces or embayments

in pyroxene grains. Platinum-group minerals enclosed by unaltered Fe-Cu-Ni sulfides are commonly subhedral. However, boundaries with hydrous silicate minerals are invariably sutured or cusped, indicating localized remobilization of the PGM associated with replacement of the sulfide. Prendergast (1990) attributed similar replacement textures of PGM in the Main Sulfide Zone of the Great Dyke, Zimbabwe to the *in situ* evolution of intercumulus silicate and sulfide liquids and a fluid phase and their continuous reaction with each other and with primary silicates.

ANALYTICAL PROCEDURE

The samples examined in this study consisted of polished blocks from the previously described mineralized zone. The compositions of most PGM had been semiquantitatively determined in the previous SEM studies of Hoatson & England (1986) and Hoatson & Keays (1989) using energy-dispersion techniques on a JEOL JSM-35 scanning electron microscope that incorporated a Robinson detector (Table 1). Each block was freshly buffed before analysis with the laser-Raman microprobe.

Raman microprobe spectra were recorded using a spectral bandpass of 3.8 cm^{-1} on a Microdil-28 Raman microprobe, previously described in detail by Liu & Mernagh (1990). The 514.5 nm line from a Spectra Physics 2020 argon-ion laser was used as the excitation source. Scattered radiation was collected at 180° using an Olympus $100\times$ (0.95 N.A.) objective and laser powers between 1 and 10 mW measured at the sample. Incident laser powers below 10 mW were required to prevent damaging the grains of PGM. Each specimen was checked for possible laser-induced damage at the completion of spectral acquisition, and data from any samples that showed discoloration or a small crater at the point of laser illumination were discarded. Multichannel spectra were typically acquired after 20 accumulations and between 5 and 30 seconds integration time. After analyzing each grain of PGM, a spectrum from a silicon standard was acquired under identical conditions. This standard had a full-width half maximum (FWHM) of 5 cm^{-1} , such that calibration was based on the band maximum at 522 cm^{-1} , but all spectra were reproducible to $\pm 1 \text{ cm}^{-1}$.

RESULTS AND DISCUSSION

The Raman microprobe spectra presented in this paper are reproducible for several different grains of the same mineral; the frequencies of the Raman bands obtained from the PGM analyzed in this study are shown in Table 2. All the observed bands lie in the region below 500 cm^{-1} , and each mineral produces a distinct Raman spectral fingerprint. Furthermore, as the Raman spectra suggest, the PGM examined in this study may be divided into two groups, those having

TABLE 2. EXPERIMENTALLY OBSERVED RAMAN FREQUENCIES FOR PLATINUM-GROUP MINERALS FROM THE MUNNI MUNNI COMPLEX

Mineral	Formula	System	Space Group ^a	Raman Bands (cm ⁻¹)						
Sperrylite	PtAs ₂	Cubic	Pa ₃ (T _h ⁶)	<u>216</u> ^b	<u>225</u> ^c	268	281	298	<u>350</u> ^d	
Platarsite	PtAsS	Cubic	Pa ₃ (T _h ⁶)	<u>214</u>		253	283	291	<u>350</u>	427
Moncheite	(Pt,Pd)(Te,Bi) ₂	Trigonal	P ₃ ml (D _{3d} ³)	<u>115</u>	155					
Cooperite	PtS	Tetragonal	P ₄ /mmc (D _{4h} ⁹)				319	<u>332</u>	347	365
Braggite	(Pt,Pd,Ni)S	Tetragonal	P ₄ /m (D _{4h} ¹³)			264		317	<u>351</u>	379
Potarite	PdHg	Tetragonal	P ₄ /mmm (D _{4h} ¹)			254	285		<u>340</u>	362

^a Space Groups in brackets are given in the Schoenflies notation.

^b Underlined wavenumbers denote peaks with stronger intensity.

^c Raman peak occurs as a shoulder on the side of the main peak.

^d Very broad, weak Raman band.

cubic or trigonal symmetry, and those with tetragonal symmetry.

PGM with cubic or trigonal symmetry

Sperrylite, platarsite and moncheite are members of this group. Sperrylite (Fig. 1B) is white with a metallic luster. It is a cubic mineral with the pyrite structure, as confirmed by Szymański (1979). A group-theory analysis of the crystal structure predicts the following irreducible representation for sperrylite: $A_g + E_g + 3F_g + 2A_u + 2E_u + 3F_u$. Only the *gerade* or "g" modes are Raman-active, whereas the *ungerade* or "u" modes are infrared-active. The Raman spectrum obtained from sperrylite is shown in Figure 2A. Five relatively sharp bands are observed in the Raman spectrum of sperrylite (see Table 2), which agrees well with the theoretical predictions. The band at 216 cm⁻¹ is much more intense than any of the other bands in the Raman spectrum. We have tentatively assigned it to the totally symmetric A_g mode. The very broad, weak band centered around 350 cm⁻¹ may arise as part of the second-order Raman spectrum, which has been previously observed in Raman spectra of sulfides (Mernagh & Trudu 1993).

Platarsite (Fig. 1C) is another cubic mineral that has a structure very similar to that of sperrylite (Szymański 1979). The bonding geometry in the two minerals is almost identical, but the bond lengths in platarsite are significantly shorter than those of sperrylite. Szymański (1979) has confirmed that the As and S atoms are randomly distributed about the octahedra surrounding the central platinum atoms. According to group theory, this structure should not give a first-order Raman spectrum, and hence, the observed spectrum (see Fig. 2B) must be the second-order Raman spectrum. This would explain the much weaker intensity of the Raman bands of platarsite and

the fact that the broad band centered at 350 cm⁻¹ is the dominant one in the spectrum. The fact that many of the observed Raman bands of platarsite occur at similar frequencies to those of sperrylite (see Table 2) also confirms the isostructural relationship between these two minerals.

Although not of cubic symmetry, moncheite gives a Raman spectrum with one very intense band at a much lower wavenumber than that of sperrylite (Fig. 2). However, the overall spectral characteristics are similar to those of sperrylite (Fig. 2), and it has, therefore, been included in this group. Moncheite (Fig. 1D) is white in polished section, with high reflectivity, and is strongly anisotropic except in sections close to (001). Factor-group analysis predicts A_{1g} and E_g Raman-active modes for this structure. Hence the broad but intense band at 115 cm⁻¹ has been assigned to the A_{1g} mode, whereas the relatively weak band at 155 cm⁻¹ has been assigned to the E_g mode. Moncheite is trigonal and is known to form a continuous solid-solution with melonite. Since melonite possesses a shorter *a* dimension than moncheite, the changes in the Raman spectrum between the two minerals are expected to be similar to the differences between sperrylite and platarsite described above.

PGM with tetragonal symmetry

Cooperite (Fig. 1E), which is dimorphous with braggite, has four atoms per unit cell and has been assigned to the D_{2h}^{16} (P₄/mmc) space group by Cabri *et al.* (1978). The structure of cooperite (PtS) is a compromise between the "square-planar" requirements of Pt²⁺ and the "tetrahedral" requirements of S²⁻, and hence, represents a distorted derivative of the sphalerite structure. Factor-group analysis predicts $B_1 + E_g$ Raman-active vibrational modes for this structure. However, the Raman spectrum of cooperite

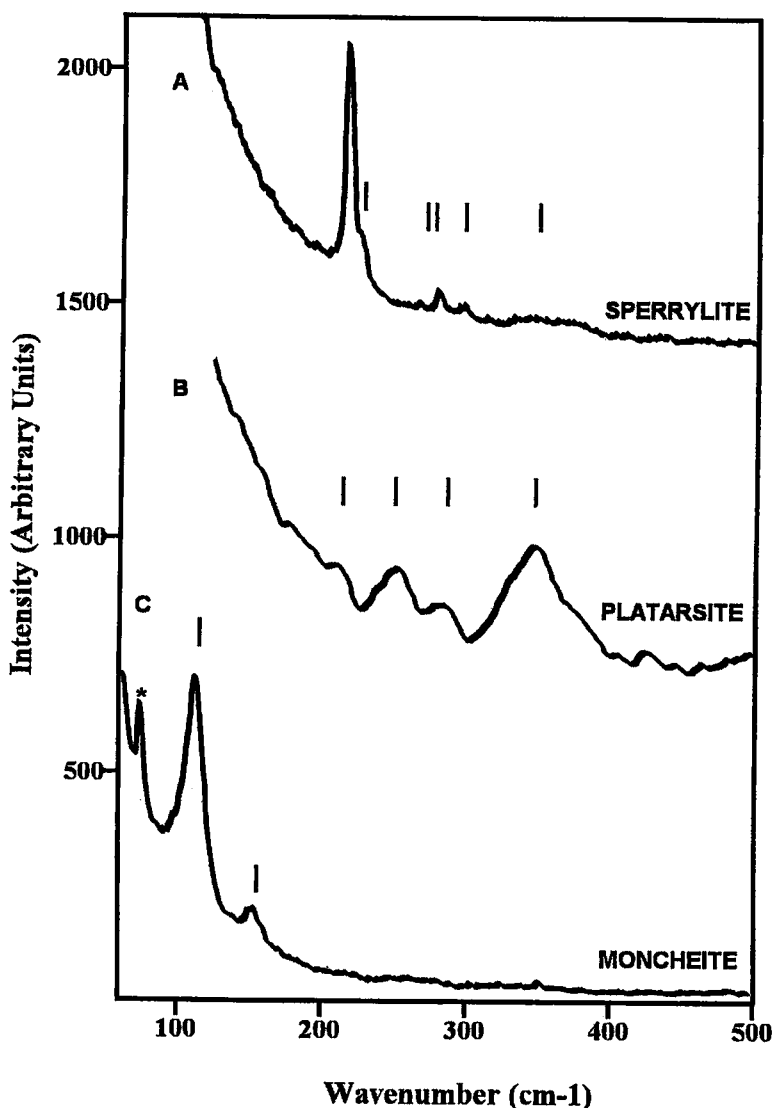


FIG. 2. Laser-Raman microprobe spectra of PGM with cubic or trigonal symmetry: sperrylite (A), platarsite (B) and moncheite (C). The vertical lines denote peaks listed in Table 2, and the star denotes a laser plasma emission.

shown in Figure 3A shows an intense band at 332 cm^{-1} with a shoulder on either side, and another broad weak band at approximately 365 cm^{-1} . The additional bands may arise from the second-order spectrum or could be due to the splitting of the original Raman band into transverse optic (TO) and a longitudinal optic (LO) modes. These can occur where the long-range forces dominate over the short-range forces in the crystal (*cf.* Mernagh & Trudu 1993). Comparison with the spectra mentioned earlier suggests that the weak broad band at 365 cm^{-1} is part of the second-order Raman spectrum.

Potarite (Fig. 1F) is a palladium amalgam initially considered to be cubic, but it was later shown to have tetragonal symmetry by Terada & Cagle (1960). This metallic amalgam should not produce a first-order Raman spectrum, and thus the bands observed in Figure 3B must be second-order. Although only a relatively weak spectrum was obtained, two distinct bands are observed, at 340 and 362 cm^{-1} , with other possible weak, broad bands at 254 and 285 cm^{-1} .

Braggite, $(\text{Pt,Pd,Ni})\text{S}$, also studied by Cabri *et al.* (1978), has 16 atoms per unit cell, belongs to space group D_{4h}^{13} ($P4_2/m$), and occurs in association with

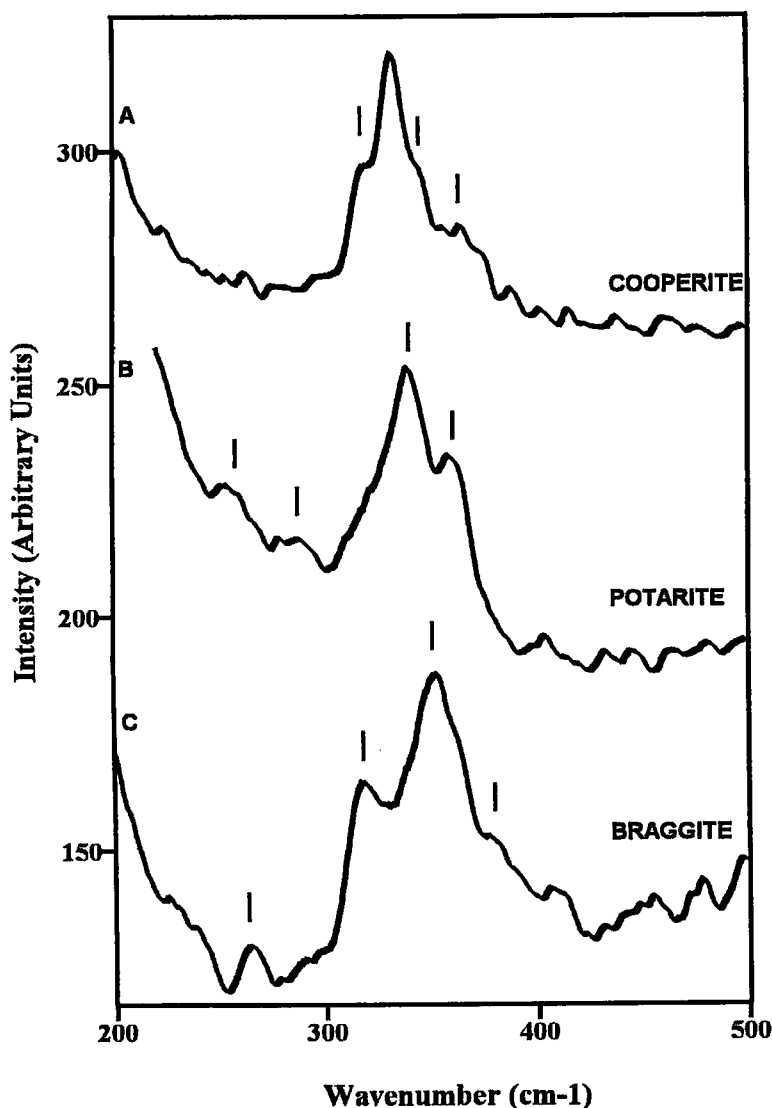


FIG. 3. Laser-Raman microprobe spectra of PGM with tetragonal symmetry: cooperite (A), potarite (B) and braggite (C). The vertical lines denote peaks listed in Table 2.

potarite in Figure 1F. The structure of braggite is essentially a superlattice of the cooperite structure, and analysis of the lattice vibrations predicts $2A_{1g} + 3B_{1g} + 2B_{2g} + 7E_g$ Raman-active modes. Broad peaks were observed at 317 and 351 cm^{-1} , with another very weak band at 264 cm^{-1} . A comparison with the Raman spectrum of cooperite shows that the dominant Raman bands have been shifted to higher wavenumbers, which is consistent with the substitution of Pd for Pt in the structure. A complete assignment of bands must await more detailed studies of spectral polarization, but the observed bands could possibly be

B_{1g} or E_g modes, by analogy with the spectrum of cooperite. However, as suggested in the Raman spectrum of sperrylite and potarite, the bands occurring around 350 cm^{-1} may also arise from the second-order spectrum. Alternatively, this spectrum may be complicated by the presence of vysotskite $[(\text{Pd} > \text{Pt}, \text{Ni})\text{S}]$, which is reported to be isostructural with braggite and PdS (*cf.* Childs & Hall 1973). Together, these minerals form the series PdS $\rightarrow$ vysotskite $\rightarrow$ braggite $\rightarrow$ cooperite in the Pd-Pt-S system. The close similarities among these minerals has previously led to confusion over their qualitative descriptions and identification by

reflected-light microscopy (*cf.* Criddle & Stanley 1985). Semiquantitative SEM analysis was used to confirm the identity of the braggite specimens used in this study, but it is possible that these grains contain minor amounts of vysotskite. Unfortunately, although vysotskite also occurs in the Munni Munni complex (Table 1), it could not be examined in this study because of possible interference from adjoining minerals owing to the small size of these grains ($<2\ \mu\text{m}$). However, grains as small as $1\ \mu\text{m}$ may be easily identified once standard spectra are available.

CONCLUSIONS

Even though more detailed studies are required for complete spectral assignments, these initial Raman spectra have shown that the differences between the Raman spectra of PGM allow the identification of these minerals by Raman spectroscopy. This technique offers the advantages of a high spatial resolution and relatively rapid identification of micrometric grains in a silicate or sulfide matrix. However, the spectra are generally weak, and care is needed to prevent laser damage to the PGM. The laser beam can also penetrate transparent crystals and hence, PGM trapped inside a transparent host-crystal also may be identified using this technique. This advantage will mean that less preparation of samples is required in many cases.

In this study of minerals from the Munni Munni Complex, the laser-Raman microprobe has been used to unambiguously identify many of the common, relatively small ($<10\ \mu\text{m}$) PGM grains hosted by either silicate or sulfide minerals. Most of the host minerals may also be positively identified with the Raman microprobe at the same time (*e.g.*, Boyer & Smith 1984, Mao *et al.* 1987, Mernagh & Trudu 1993). As this is also a structure-sensitive technique (Mernagh & Trudu 1993), it can discriminate between polymorphs and identify structurally anomalous crystals. This technique of vibrational spectroscopy does not provide a chemical composition, so that an electron or proton microprobe is still required to obtain these data. However, the laser-Raman microprobe provides a relatively convenient and rapid technique for the positive identification of PGM within a specimen or thin section, in comparison with the more commonly used techniques, such as electron-microprobe or X-ray diffraction.

ACKNOWLEDGEMENTS

We thank Louis Cabri and an anonymous referee, as well as Greg Ewers and Hashem Etninan, for helpful comments and suggestion on an earlier draft of this manuscript. The authors publish with the permission of the Executive Director of the Australian Geological Survey Organisation.

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Received May 30, 1994, revised manuscript accepted September 12, 1994.