ARGENTIAN PENTLANDITE WITH PARKERITE, JOSEITE A AND THE PROBABLE BI-ANALOGUE OF ULLMANNITE FROM MOUNT WINDARRA, WESTERN AUSTRALIA

D. I. GROVES & S. R. HALL

Department of Geology and Crystallography Centre, University of Western Australia, Nedlands, Western Australia 6009

ABSTRACT

At Windarra, in the greenstone sequence beneath the major nickel mineralization, argentian pentlandite occurs within quartz-sulfide veinlets containing pyrrhotite, chalcopyrite, galenobismutite, native Bi, parkerite, pentlandite, pyrite, galena, sphalerite, joseite A and the probable Bi-analogue of ullmannite. Both parkerite and joseite A are Pb-poor varieties, whereas the Bi-analogue of ullmannite contains significant Pb. Argentian pentlandite occurs as an exsolution phase in chalcopyrite and possibly as a replacement of pyrrhotite and pentlandite in association with Bi- and Pb-rich phases. It has a composition Fe_{0.5}Ni_{0.6}Ag_{<0.1} and contains less than 0.1 wt% Co. It coexists with pentlandite containing 0.8% Co and less than 0.1% Ag. The low Co content of argentian pentlandite may reflect exsolution from Co-free chalcopyrite. From all published analyses, argentian pentlandite has the general formula \((Fe^{2+}_{3+2.5x}Ni_{3+2.5x})_{\delta+2Ag_{0.5}S_8}\) where \(0 < x < 0.2\), and the \(Fe/Ni\) ratio may be even more limited if possible analytical errors are considered. Despite the wide range of reported parageneses, the restricted range of \(Fe/Ni\) ratio in argentian pentlandite, as compared to pentlandite, suggests the possibility that Fe and Ni may occupy specific tetrahedral sites in a structure with space group \(P43m\).

INTRODUCTION

Small sulfide veinlets from a drill core cutting the greenstone sequence underlying the Windarra nickel deposit in Western Australia contain...
an unusual Bi- and Ni-rich assemblage of the first documented Australian occurrences of argentian pentlandite and parkerite.

Argentian pentlandite was first described by Shishkin et al. (1971) from U.S.S.R., and by Vuorelainen et al. (1972) from Finland and subsequently reported by Scott & Gasparrini (1973) and Karpenov et al. (1973). The crystal structure of argentian pentlandite was determined by Hall & Stewart (1973) and the stability and phase relations were described by Mandziuk & Scott (1977). Although argentian pentlandite may occur as a minor phase in Ni-Cu ores, it seems to occur more commonly in peripheral mineralization closely associated with chalcopyrite-rich assemblages.

Parkerite has a very limited occurrence, previously being recorded from Insizwa, South Africa (Scholtz 1936) and a few localities in Canada: Sudbury (Michener & Peacock 1943), Great Slave Lake (Thompson 1951) and Langis mine, Cobalt-Gowganda area (Petruk et al. 1969). Its structure has been examined by Fleet (1973) and Brower et al. (1974). Like argentian pentlandite, parkerite occurs as a minor component of peripheral mineralization or in hydrothermal veins rather than within the usual assemblage of Ni-Cu ores. It is commonly associated with native Bi, (Ni,Co) arsenides, pentlandite and chalcopyrite.

GEOLGICAL SETTING OF THE OCCURRENCE

The Windarra deposit, approximately 23 km northwest of Laverton, Western Australia, is a metamorphosed Fe-Ni sulfide deposit in a metamorphosed ultramafic sequence, associated with metasedimentary rocks and amphibolites in a wedge-shaped greenstone belt between two deformed granitoid plutons (Robinson et al. 1973; Robert 1975; Seccombe et al. 1977). The main deposits consist of disseminated ore, with minor breccia and massive ore that contain a monotonous hypogene assemblage of pyrrhotite, pentlandite, chalcopyrite, pyrite and chromian magnetite with minor sphalerite, rare galena, and (Ni,Co,Fe) sulfarsenides.

The mineralization described here occurs in a single drill core (N309) at 1074 m beneath the main footwall banded iron-formation; it consists of small quartz-rich patches containing sulfide veinlets and patches (up to 10×8×5 mm) adjacent to a felsic dyke. This, combined with the transgressive nature of the mineralization and apparent lack of deformation of the sulfides (cf., main ore zone; Seccombe et al. 1977), suggests that the mineralization may have a hydrothermal origin related to dyke emplacement, although the isolated occurrence means that any proposed origin must be equivocal. Irrespective of origin, the argentian pentlandite- and parkerite-bearing assemblage is peripheral to the main nickel mineralization, a feature common to several such occurrences.

SULFIDE PARAGENESIS (EXCLUDING ARGENTIAN PENTLANDITE)

Textural relationships

The sulfide aggregates consist of complex intergrowths of the following minerals, in approximate order of abundance: pyrrhotite, chalcopyrite, galenobismutite, native Bi, parkerite, pentlandite, argentian pentlandite, pyrite, galena, sphalerite, joseite A and the probable Bi-analogue of ullmannite. Within the sulfide aggregates, some areas are dominated by Bi- and Pb-rich phases, others by pyrrhotite ± chalcopyrite. Although textural relationships are equivocal, an early-formed assemblage of pyrrhotite + pentlandite + chalcopyrite + pyrite seems to have been rimmed and replaced by the Bi,Pb-rich assemblage and chalcopyrite, with which all of the parkerite and most argentian pentlandite are associated.

Areas dominated by pyrrhotite consist of discrete grains up to 4mm diameter, either intergrown with coarse-grained chalcopyrite or poikilitically enclosing pentlandite grains (0.2mm mean diameter) or symplectite-like chalcopyrite-pyrite intergrowths (range 0.1 to 0.4mm diameter) or both. Coarser-grained pentlandite, up to 1mm diameter, occurs on the margin of pyrrhotite-dominated sulfide aggregates that are normally rimmed by complex intergrowths of galenobismutite, native Bi and galena or parkerite; the latter occurs either as discrete grains or as irregular inclusions with or without native Bi rims in marginal pentlandite. Sphalerite occurs as small blebs (0.05mm diameter) in both chalcopyrite and pyrrhotite.

Areas rich in Bi and Pb sulfides consist of aggregates of galenobismutite grains (up to 3mm diameter) enclosing irregular aggregates of native Bi, commonly in a symplectite-like intergrowth with galena (Fig. 1); the native Bi and galena seem to be a replacement product of galenobismutite. Twinned aggregates of parkerite commonly enclose native Bi-galena intergrowths, and occur as irregular lenses in galenobismutite or are themselves rimmed by intergrowths of native Bi and galena. Small flame-like bodies of joseite A occur at the ex-
tremities of some parkerite lenses, or as discrete bodies in galenobismutite. One small flame-like body in galenobismutite is tentatively identified as the Bi-analogue of ullmannite, but its small size (0.5×0.05mm) makes precise identification of optical properties impossible. It has a bluish-grey tint relative to galenobismutite, a similar reflectivity to galenobismutite and is isotropic: its properties thus suggest ullmannite.

**Compositional data**

The sulfides were analyzed on a MAC 4005 electron microprobe at CSIRO Division of Mineralogy, Western Australia. Operating conditions were 19.3 kV and 10-11μA specimen current. The following standards were used: pyrite for Fe and S, galena for Pb, and Co, Ni, Ag, Bi and Te metals. Data were computed on-line using the program MAGIC 4 (Colby 1971). Analyses are presented in Table 1 and all formulae are calculated on the basis of a fixed number of sulfur atoms.

Parkerite has a relatively constant composition throughout the sulfide aggregates, approximating Ni_{0.03}Bi_{0.07}S_{2}, i.e., close to the ideal composition of the Ni_{0.9}Bi_{0.1}S_{2} end-member of the Ni_{0.9}Bi_{0.1}Pb_{0.1} solid-solution series (Peacock & McAndrew 1950). Its composition is thus similar to that from the Cobalt area recorded by Petruk et al. (1969), but contains less Pb than does parkerite from Sudbury and Insizwa (Michener & Peacock 1943; Scholtz 1936).

Joseite A also has a relatively constant composition approximating Ni_{0.03}Pb_{0.07}Bi_{0.1}Te_{0.9}S_{3}, thus corresponding reasonably well to the idealized formula Bi_{n+1}Te_{1+n}S_{2n}. The composition is similar to that from central Asia recorded by Mintser et al. (1968) but contains significantly less Pb than that recorded by Harada et al. (1972) from Japan. An interesting feature is its consistent but low Ni content, even where joseite is remote from parkerite.

The single analysis of the Bi-analogue of ullmannite(?) (Table 1, no. 6) can be regarded as semiquantitative only: the small flame-like inclusion is enclosed in galenobismutite and fluorescence problems during analysis are inevitable. However, Ni_{0.9}Pb_{0.1}Bi_{0.1}S corresponds very closely to the expected ideal composition Ni(Bi,Pb)S. We believe that this is the first recorded occurrence of the Bi-analogue of ullmannite, although Bi-rich varieties of ullmannite (kallilite) are known (Uytenbogaardt & Burke 1971). The data are insufficient at this stage to permit complete characterization of this phase for submission to the IMA.

**Reflectivity and hardness data**

The reflectivity of parkerite was determined using a Leitz Mikroskop – Photometer MPV attached to a Leitz Orthoplan microscope at the National Institute of Metallurgy, Johannesburg, South Africa. A WTIC standard, and 20X and 50X objectives were used in the measurements. The results (Table 2) are compared with the data of Petruk et al. (1969), the only other published reflectivity measurements. In view of the strong anisotropism, there are no significant differences between the data.

The Vickers hardness data of parkerite (Table 2) were measured using a Leitz Durimet instrument at the Department of Geology, University of the Witwatersrand, Johannesburg, South Africa. These values are lower than the values of 111-142 kg/mm (125 mean) obtained by Pe-

<table>
<thead>
<tr>
<th></th>
<th>1</th>
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<th>4</th>
<th>5</th>
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<td>Fe</td>
<td>35.2</td>
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<td>30.2</td>
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<tr>
<td>Co</td>
<td>0.1</td>
<td>0.1</td>
<td>0.8</td>
<td>&lt; 0.1</td>
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<td>-</td>
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<tr>
<td>Ni</td>
<td>19.9</td>
<td>19.9</td>
<td>35.5</td>
<td>26.1</td>
<td>0.5</td>
<td>18.8</td>
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<tr>
<td>Ag</td>
<td>13.1</td>
<td>11.0</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>0.1</td>
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<tr>
<td>Pb</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt; 0.1</td>
<td>1.7</td>
<td>15.3</td>
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<tr>
<td>Bi</td>
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<td>-</td>
<td>-</td>
<td>63.6</td>
<td>80.2</td>
<td>56.0</td>
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<td>Te</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>12.1</td>
<td>-</td>
<td>-</td>
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<td>S</td>
<td>31.2</td>
<td>30.3</td>
<td>32.2</td>
<td>9.6</td>
<td>6.2</td>
<td>10.6</td>
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<td>TOTAL</td>
<td>99.5</td>
<td>99.1</td>
<td>99.7</td>
<td>99.5</td>
<td>100.8</td>
<td>100.7</td>
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1. Argentian pentlandite in parkerite - bismuth assemblage
2. Argentian pentlandite in pyrrhotite - chalcopyrite assemblage
3. Pentlandite in pyrrhotite
4. Parkerite in galenobismutite
5. Joseite A in galenobismutite
6. Bismuth analogue of ullmannite (?)
   - Not determined

**Fig. 1.** Cube of argentian pentlandite (apn: dark grey) enclosed in a symplectite-like intergrowth of bireflectant bismuth (light grey) and galena (gn: medium grey). Width of field 0.5mm.
text.

truk et al. (1969), but considering the variations in both sets of measurements, it is difficult to assess whether the differences are significant.

ARGENTIAN PENTLANDITE

Textural relationships

Argentinian pentlandite occurs both in the pyrrhotite-dominated aggregates and in the Bi- and Pb-rich aggregates. It is reddish-brown, isotropic, and without visible cleavage, as described by most authors, although Vuorelainen et al. (1972) have observed cleavage in some grains. Argentinian pentlandite occurs around the margins of pyrrhotite grains where it may be present as discrete grains, as complex intergrowths with pyrrhotite, or in symplectite-like intergrowths of Bi and galena. Some individual grains also contain inclusions of native Bi, galena and galenobismutite. Argentinian pentlandite also occurs as irregular rims on parkerite-dominated grain aggregates, but is rarely in contact with pentlandite, except as vein-like bodies replacing pentlandite along cleavages (cf., Shishkin et al. 1971) or with parkerite as inclusions in pentlandite. Most grains are anhedral, but crystal faces are developed in some cases: sections through subhedral to euhedral grains are cubic (Fig. 1) or probably octagonal (Fig. 2) as described by Karpenov et al. (1973).

A most interesting association is found with chalcopyrite. The argentian pentlandite is commonly included within chalcopyrite as irregular patches or elongate bleb-like forms. In places it forms regular intergrowths with chalcopyrite (Fig. 3), or symplectite-like intergrowths with pyrite (Fig. 4) identical to those exhibited by chalcopyrite and pyrite. This texture is typical of Western Australian nickel ores and is interpreted to result from subsolidus reaction between Cu-Fe-S intermediate solid solution (iss) and pyrite (Barrett et al. 1977). Small blebs of sphalerite that contain minute exsolution bodies of chalcopyrite, identical to those occurring within adjacent chalcopyrite, are rarely present in argentian pentlandite. These features confirm previous suggestions (Shishkin et al. 1971; Vuorelainen et al. 1972; Scott & Gasparrini 1973; Mandziuk & Scott 1977) that argentian pentlandite may exsolve either from chalcopyrite, which has a similar structure with sulfur cubic close-packing (Hall & Stewart 1973), or from a Ag-bearing Cu-Fe-S iss.

Compositional data

Compositional data for argentian pentlandite and co-existing pentlandite are given in Table 1 (nos. 1, 2, 3) and calculated compositions of Windarra argentian pentlandites are compared

<table>
<thead>
<tr>
<th>Reflectance (nm)</th>
<th>460</th>
<th>546</th>
<th>589</th>
<th>640</th>
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<tr>
<td>Windarra (5 readings)</td>
<td>min. 43.0-43.8</td>
<td>44.6-45.2</td>
<td>45.0-45.8</td>
<td>45.8-46.0</td>
</tr>
<tr>
<td>max. 46.5-47.3</td>
<td>48.3-49.1</td>
<td>48.8-50.0</td>
<td>50.0-50.9</td>
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<tr>
<td>Cobalt (4)</td>
<td>min. 43.4-44.0</td>
<td>43.5-43.9</td>
<td>44.0-44.4</td>
<td>45.2-46.2</td>
</tr>
<tr>
<td>max. 44.7-47.7</td>
<td>47.3-47.9</td>
<td>47.6-48.5</td>
<td>48.0-49.5</td>
<td></td>
</tr>
<tr>
<td>Tin (3)</td>
<td>min. 42.0-44.7</td>
<td>44.0-46.1</td>
<td>44.2-44.8</td>
<td>47.5-47.6</td>
</tr>
<tr>
<td>max. 44.0-46.3</td>
<td>44.6-46.9</td>
<td>48.4-46.6</td>
<td>49.5-49.5</td>
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</table>

Vickers Hardness:

<table>
<thead>
<tr>
<th>Windarra (62 - 126 kg/mm², mean 97)</th>
<th>25g load</th>
</tr>
</thead>
<tbody>
<tr>
<td>62 - 106 kg/m², mean 97</td>
<td>50g load</td>
</tr>
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</table>

Fig. 2. Section through a probable octagonal argentian pentlandite grain (apn: dark grey) enclosed in bismuth (light grey) and galenobismutite (gnb: medium grey), which also occur as small inclusions in argentian pentlandite. Width of field 0.12mm.

Fig. 3. Regular intergrowth of argentian pentlandite (apn: dark grey) and chalcopyrite (cpy: light grey) enclosed in pyrrhotite (po: medium grey). Width of field 0.1mm.
with other argentian pentlandites in Table 3. The composition falls very close to the ideal formula (Fe,Ni)₅AgS₆, comparing well with the data of Hall & Stewart (1973). No analyzed grains had metal : sulfur ratios in excess of 9.2:8.0, in agreement with Karpenov et al. (1973), Scott & Gasparrini (1973) and with all but one analysis by Shishkin et al. (1971). As in most previously analyzed argentian pentlandites where there is approximately one silver atom per formula, the Ag apparently occupies the 4b octahedral sites in the crystal structure.

As also recorded by Vuorelainen et al. (1972) and indicated by the analyses of Hall & Stewart (1973), the argentian pentlandite from Windarra contains very little Co, in contrast to the co-existing Ag-free pentlandite (Table 1). The low Co content cannot be explained by restriction of Co to the octahedral sites already occupied by Ag, because many pentlandites contain Co:S ratios in excess of 1:8 (e.g., Vuorelainen et al. 1973). The low Co contents could be explained by exsolution of argentian pentlandite from essentially Co-free chalcopyrite (or iss), or by crystallization from a Co-poor solution: the former appears more generally applicable, as the association of argentian pentlandite with chalcopyrite is widespread.

The additional data from Windarra further emphasize the limited Fe/Ni ratio of argentian pentlandites compared to pentlandites (e.g., Harris & Nickel 1972; Misra & Fleet 1973) despite the wide range of assemblages from which the occurrences have been recorded. All analyzed argentian pentlandites fall into the compositional range (Fe₃₋₁₋₀.₄Ni₁₋₀.₄)ₓ₋₀.₄Ag₁₋₀.₄S₆, 0<x<0.2; in reality this range could be smaller, as the extreme deviations from a formula of Fe₃Ni₄AgS₆ are those with high metal/sulfur ratios (e.g., analyses 5 and 7, Table 3). This suggests the possibility that the Fe and Ni may occupy specific tetrahedral sites within the argentian pentlandite structure.

Reflectivity and hardness data

The reflectivity data for argentian pentlandite, determined using the equipment described above, are compared with published values in Table 4. Our measurements fall within, or close to, the range of the published data.

Our Vickers hardness data for argentian pentlandite (Table 4) compare favorably with the values of Scott & Gasparrini (1973), Vuorelainen et al. (1972) and Shishkin et al. (1971), taking into consideration that apparent hardness generally increases with decreasing load.
TABLE 4. REFLECTANCES AND VIKERS HARDNESS OF ARGENTIAN PENTLANDITE

<table>
<thead>
<tr>
<th>% Reflectance</th>
<th>450 nm</th>
<th>546 nm</th>
<th>546 nm</th>
<th>589 nm</th>
<th>640 nm</th>
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<tbody>
<tr>
<td>Windarra (5)</td>
<td>26.6 - 29.3 (29.11)</td>
<td>33.6 - 34.2 (34.01)</td>
<td>36.8 - 37.2 (37.01)</td>
<td>39.6 - 40.2 (39.91)</td>
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<tr>
<td>Scott &amp; Capacci (1973)</td>
<td>546 nm</td>
<td>546 nm</td>
<td>589 nm</td>
<td>640 nm</td>
<td></td>
</tr>
<tr>
<td>Voureniau et al. (1972)</td>
<td>26.3</td>
<td>37.14 (7)</td>
<td>33.0</td>
<td>39.8</td>
<td></td>
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<tr>
<td>Shlikin et al. (1972)</td>
<td>30.3</td>
<td>35.5</td>
<td>36.5</td>
<td>38.6</td>
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<tr>
<td>Karpfenov et al. (1973)</td>
<td>26.1</td>
<td>33.9</td>
<td>35.5</td>
<td>37.4</td>
<td></td>
</tr>
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</table>

Vickers Hardness

Windarra (5 readings): 144 - 152 kg/mm² at 100 & 200g load
Scott & Capacci (1973): 139 - 170 kg/mm² at 100g load
Voureniau et al. (1972): 132 - 154 kg/mm² at 50g load
Shlikin et al. (1971): 162 - 173 kg/mm² at 10g load

(Hardness generally increases with decreasing load).

SUMMARY

At Windarra, argentian pentlandite occurs in a previously unrecorded Bi- and Pb-rich association that includes the rare minerals parkerite and joseite A. It appears as a late-stage phase partly exsolved from chalcopyrite and partly introduced with native Bi, galena, galenobismuthite and parkerite as a replacement of pyrrhotite and pentlandite. Argentian pentlandite is the only Ag-bearing mineral of the assemblage. Its optical properties and Vickers hardness agree with those described by most previous authors. A low Co content with respect to coexisting pentlandite may reflect an origin by exsolution from Co-free chalcopyrite. The metal:S ratio, almost exactly 9:8, and the Ag:S ratio, exactly 1:8, confirm previous suggestions that Ag occupies only the octahedral sites. The composition of argentian pentlandite is close to Fe₅Ni₃AgS₆ in agreement with most other reliable microprobe analyses, suggesting that Fe and Ni may occupy specific tetrahedral sites. The structure of argentian pentlandite may thus be based on the primitive space group P43m, instead of the face-centred space group Fm3m, although X-ray diffraction is unlikely to discriminate between these alternatives.

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