PRECIOUS METALS IN VOLCANIC-TYPE NICKEL SULFIDE DEPOSITS IN WESTERN AUSTRALIA

I. RELATIONSHIP WITH THE COMPOSITION OF THE ORES AND THEIR HOST ROCKS

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ABSTRACT

We examine the relationship between the bulk composition of the sulfide fraction and the abundances of Pd, Pt, Ir and Au in volcanic-type nickel sulfide deposits of Western Australia. We also review abundance of these elements in samples representing the liquid and olivine components of the komatiitic ultramafic sequences that host the deposits. Results from representative samples of ore, recalculated to 100% sulfides, show varying degrees of positive correlation between the tenor of precious metals and the Ni content. The correlation is good for Ir and Pd and weak to moderate for Pt, whereas Au values show no regular trends. Our study of ore profiles, sulfide stringers and mineral separates, however, has shown us that considerable effort and care is required to establish average precious metal values in volcanic-type deposits. Samples representing the high-Mg liquid fraction of the magmas that coexisted with original sulfide melts have Pd:Ir ratios similar to those of the sulfides; this fact indicates that these liquids exerted the dominant influence on the relative partitioning of precious metals between silicate magmas and sulfide melts. A wide range of sulfide-melt compositions were associated with only a narrow range of silicate-melt compositions; factors other than the bulk composition of the silicate melt controlled the composition of the sulfide melt.

INTRODUCTION

We have addressed five questions relating to volcanic-type nickel sulfide deposits at Kambalda and elsewhere in Western Australia: (1) how should these orebodies be sampled to determine their precious-metal contents? (2) what is the relationship between the abundance of precious metals in different ore zones and the composition of the ores? (3) what is the relationship between the precious-metal contents of the ores and their host rocks? (4) what is the distribution of precious metals in individual sulfide phases? (5) what can precious metals tell us about the influence of metamorphism on the composition and distribution of the sulfide ores?

More than 1400 individual precious-metal analyses have been generated during this project and results are presented in two parts. Part I
(this paper) places emphasis on the relationship of Pd, Pt, Ir and Au to the composition of ores and host rocks, and on their partitioning between original silicate and sulfide melts. A companion paper (Part II: Keays et al., in prep.) examines the distribution of precious metals within ore zones and host rocks at Kambalda in more detail, including their partitioning between sulfide minerals and between original silicate phases.

**Geological Setting**

Nearly all of the nickel sulfide deposits in Australia occur in Archean greenstone belts within the Eastern Goldfields province of the Yilgarn Block (Fig. 1), mostly within the Norseman–Wiluna belt as defined by Williams (1973). Apart from a few exceptions (e.g., Carr Boyd: Schultz 1975), these deposits are associated with the komatitic ultramafic members of the greenstone belts (an association discussed more fully by Naldrett & Cabri 1976). Two principal types of deposit are recognized: (1) the volcanic type (Binns et al. 1977), typified by thin layers of matrix and massive sulfides at, or near, the base of lenses of altered olivine peridotite up to 50 m thick. These lenses usually

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**Fig. 1.** Generalized geological map of the Yilgarn Block of Western Australia showing the greenstone belts and the location of the principal nickel sulfide deposits. Those mentioned in text include Kambalda, Forrestania (F), Nepean (N), Redross (R), Scotia (Sc), Spargoville (S), and Windarra (W).
occur at the bottom of much thicker sequences of komatiitic ultramafic flows with lower MgO contents. The volcanic-type deposits rarely contain more than 5 million tonnes and usually less than 2 million tonnes of ore. Most have average ore-reserve grades of $\geq 2\%$ Ni and Ni:Cu ratios of 10–15:1; (2) the dunitic type, typified by internal low-grade disseminations of sulfides within altered dunitic bodies up to 900 m thick (e.g., Mt. Keith: Burt & Sheppy 1975), but deposits with higher grade, near-contact accumulations of sulfides (e.g., Perseverance: Martin & Allchurch 1975) form a substantial part of the nickel metal reserves in this class. Individual deposits contain up to 263 million tonnes of ore (Mt. Keith) with average grades commonly about 0.6% Ni; Ni:Cu ratios usually occupy the range 25–60:1.

There is widespread acceptance of a magmatic origin for essentially all of the sulfides in these deposits, even though both ore and host rocks have been metamorphosed to grades ranging from greenschist to upper amphibolite facies (Binns et al. 1977). Initial studies of

Fig. 2. Geological plan of the Kambalda Dome.
volcanic-type deposits (Ewers & Hudson 1972, Hudson 1972, Ross & Hopkins 1975) regarded both matrix and massive sulfides as the product of magmatic accumulation, but recently Binns et al. (1977) and Barrett et al. (1977) have argued for the generation of massive ores from disseminated sulfides in some environments of dynamic-style metamorphism (e.g., Nepean, Windarra) and implied that similar processes occurred in environments of static-style metamorphism such as Kambalda.

The regional setting of the Kambalda district has been illustrated by Gemuts & Theron (1975), whereas the district geology and ore deposits have been described by Woodall & Travis (1969), Ross (1974), and Ross & Hopkins (1975). Most of the deposits are clustered around the Kambalda Dome, at the outwardly dipping, correct-facing contact between a footwall of tholeiitic metabasalt and an overlying sequence of komatiitic ultramafic rocks up to 800 m in thickness (Fig. 2). The lower portion of this sequence consists of thick units (usually 10–50 m in thickness) of metacumulate peridotite (commonly 34–45% MgO) which are in turn overlain by multiple thin units (<10 m) of metacumulate and metamorphic peridotite that average about 30% MgO. (Note that all oxide and element abundance are expressed on a volatile-free basis, in recognition of the large, variable component of CO₂ and H₂O in altered ultramafic rocks.) Both types of units commonly show chill margins and spinifex textures in the upper sections, and the sequence is regarded as essentially extrusive. About 85% of the pre-mining reserves of nickel metal occurs in ribbonlike ore zones in direct contact with the footwall basalt and are referred to as contact ores. Typical contact ore zones show a layer of matrix sulfides, up to 2 m thick, overlying a thinner and less continuous layer of massive sulfides, which rest directly on

<table>
<thead>
<tr>
<th>TABLE 1. METAL VALUES IN 18 COMPOSITE SAMPLES OF QUOTED ORE FROM KAMBALDA AND HINISKIN, AND A KAMBALDA HEAD SAMPLE.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ore Sample</strong></td>
</tr>
<tr>
<td>LIZNAM</td>
</tr>
<tr>
<td>LUSNAM</td>
</tr>
<tr>
<td>FISHER</td>
</tr>
<tr>
<td>JUAN</td>
</tr>
<tr>
<td>KEN</td>
</tr>
<tr>
<td>DURKEN</td>
</tr>
<tr>
<td>NEPAN</td>
</tr>
<tr>
<td>KAMBALDA HEAD</td>
</tr>
</tbody>
</table>

(a) Mean values, weighted for tones.

(b) Mean values recalculated to 100% sulfides.

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(1) Ni, Cu, Co, and S expressed in wt.%; Pd, Ir, and Au in ppm. All analyses by W.M.C. unless indicated otherwise. (2) Standard deviation in parentheses. (3) Composite sample of total Kambalda mill feed, unrelated in time to the composite samples for individual ore shoots. Precious metal analyses from Kenny & Davidson (1976). (4) All values have been calculated from Si:S ratios, except for the second set of data for McMahon & Ken (see F5). (5) Recalculations based on Ni values selected on the basis of mine experience and routine specific-gravity measurements on ore. The higher S values reflect incorporation of sulfide-bearing sediments in ore during mining.
footwall basalt. The footwall basalt adjacent to
the contact often contains thin stringers of
chalcopyrite-rich sulfides. The sulfides in the
ore zones have been recrystallized and the
massive layer has experienced varying degrees
of remobilization. Some contact ore zones are
overlain by one or more zones of sulfide min-
eralization within the lower third of the overlying
ultramafic sequence. This hanging-wall mineral-
ization occurs at, or close to, the base of
ultramafic units; although it can show most of
the features of contact ore it usually consists
of thin, elongate zones of disseminated and
blebby sulfides. The collective term shoot em-
braces all zones, including hanging wall, within
each of the ore environments at Kambalda.
This description of the Kambalda deposits is
representative of the other volcanic-type de-
posits included in this study.

An important but not well recognized feature
of the volcanic-type deposits is the variation in
composition of the sulfide fraction of different
ore zones. The composition of the sulfide frac-
tion of an individual ore zone is relatively
constant over its areal extent, but it is usually
different from that of other ore zones. Most
ore shoots at Kambalda contain only one zone
of contact ore which is usually dislocated by
faulting. Where hanging-wall ore zones are pre-
sent they show a different composition of sulfide
fraction. Normal pyrrhotite–pentlandite contact
ore zones at Kambalda have S:Ni values in
the range of 2.2–4.3:1, corresponding to nickel
values of about 9 to 18% in 100% sulfides;
most of that range is represented in this study.
Lower S:Ni values at Kambalda are associ-
ated with the millerite-bearing ores at Otter Shoot
(Keele & Nickel 1974) and Gibbs Shoot, but as
they have been adequately sampled, the
compositional range has been extended by the
inclusion of material from the nickel-rich pent-
landite–pyrrhotite ores at Nepean and Scotia
(S:Ni values of about 1.8:1 and 1.6:1, respec-
tively).

**Analytical Methods**

Samples analyzed at the University of Mel-
bourne were carefully cleaned and crushed in a
soft iron mill known to have low precious-
metal contents. Gold, Ir, Pd and Co were de-
termined by a neutron-activation-analysis
(NAA) procedure modified after that of
Crocket et al. (1968) and Keays et al. (1974).
The accuracy of the method is estimated to
be ±15%; a comparison of analytical data
for some rock standards with published data
may be found in Shaw et al. (1976). Cu and
Ni were measured by AAS and S by a Leco
automatic S titrator. Whole-rock silicate an-
alyses (MgO) were obtained by XRF analysis
following the method of Haukka & Thomas

Precious-metal determinations by Western
Mining Corporation (WMC) follow the stand-
ard method for spectrographic analysis of ores,
minerals and rocks by the fire-assay precon-
centration technique (ASTM E400–71) de-
scribed in the 1971 Annual Book of ASTM
Standards; good comparative results were ob-
tained with six other laboratories. Ni, Cu and
Co were determined by AAS and routine pre-
cision is no less than ± 5% for Ni and Cu and
slightly higher for Co. Sulfur was measured by
the barium sulfate gravimetric technique with
a quoted accuracy of ± 3%.

**Precious Metals in Nickel Sulfide Ores**

Four types of samples were obtained: re-
presentative samples of ore production, re-
presentative sampling of drill core across ore
zones, samples across ore profiles at Lunnon
Shoot, and mineral separates from massive ore.

*Samples of ore production*

Ore is produced from several shoots at
Kambalda and sampled separately by ore source
at the weighbridge during transit to the primary
crusher. This procedure takes a sample of ap-
proximately 50 kg from every 50–100 tonnes
of ore. At the close of every 4-week period a
composite sample representing total production
for that period is prepared for each ore source.
During 1974–76, a total of 18 composite samples
from each of seven ore shoots were analyzed
for Pt, Pd and Au. Six of these shoots (Lunnon,
Juan, Durkin, Ken, Fisher and McMahon) are
at Kambalda (Fig. 2) and the seventh is the
nearby deposit at Nepean (Fig. 1). The ton-
nage-weighted means for the 18 samples from
each shoot are recorded in Table 1a, together
with data for a composite sample of ore produ-
cion from all sources at Kambalda collected
in 1973. Table 1b shows these values normal-
ized to 100% sulfides on the bases of S:Ni
ratios, sulfide-mineral compositions (Ewers &
Hudson 1972, Nickel et al. 1974) and pyrite
content (Woolrich & Giorgetta 1978).

Recalculation of analytical data for the sul-
fide component of nickel sulfide ores to 100%
sulfides is essential in any comparison between ore sources because absolute values in individual samples and ore production samples can be influenced more by the intensity of sulfide mineralization (e.g., disseminated, matrix or massive) and host-rock dilution during mining than by the composition of the sulfide fraction. Five features of Table 1 should be noted: (1) the ore mined from Juan, Durkin, Ken, Nepean and McMahon Shoots is essentially from a single ore-zone in each case: hanging wall at McMahon, contact at the other four. Production from Lunnon and Fisher shoots, however, was a composite of both contact and hanging-wall ore zones in different production periods, and therefore the mean data in Table 1 for these shoots should be viewed as a new composite-ore zone; (2) as the ore mined from Ken and McMahon Shoots is known to have included significant amounts of nickel-poor, pyrite- and pyrrhotite-bearing metasedimentary rock, the recalculation has been based on a value for nickel in 100% sulfides more consistent with extensive mine sampling and specific-gravity measurements on ore. The close similarity of Pd and Pt values in Lunnon and McMahon Shoots supports this adjustment; (3) calculation of the weighted mean values in Table 1a assumes a constant specific gravity for ore sampled in each of the 18 composite samples. Although this assumption is incorrect, the relatively small standard deviations for Ni and S indicate a fairly constant sulfide content; (4) the mean values have been derived from large tonnages of ore and should be representative; (5) supergene ore from the violarite-pyrite zone (Nickel et al. 1974) formed a significant part of the sampled production from McMahon, Ken and Durkin Shoots and this supergene ore may have been enriched in Pd and Pt in addition to Ni.

Values for Pd and Ni from Table 1b, plotted in Figure 3, show a positive correlation with $r = 0.88$. Figure 3 also shows the envelope covering practically all of the 18 individual composite sample results for Lunnon, Juan, Durkin and Nepean Shoots; considerable scatter is evident even though individual samples represent up to 90,000 tonnes of ore. The mean values for Pt in Table 1b have been plotted against Ni in Figure 4. They show a weaker correlation ($r = 0.53$) and the scatter of individual samples is far greater. No correlation is evident between Au and Ni, but the large discrepancy between the Au value in the Kambalda head sample, derived from NAA results, and the other mean values in Table 1b has cast doubt on all Au values in Table 1.
Other ore samples

One of us (R.K.) obtained representative drill core of contact ore zones at Redross, Nepean, and from the dunitic-type deposit at Forreastinia. Where possible, results for individual core samples have been weighted by sample length and sulfide content (a measure of specific gravity) to give the weighted mean values recorded in Table 2. These mean values have then been normalized to 100% sulfides on the basis of S:Ni ratios (Table 2b). Table 2 also includes data for the unclassified komatiitic deposits of Shangani and Hitura, for the tholeiitic deposits at Sudbury and Noril'sk, and for samples of concentrate from the volcanic-type deposits at Windarra (Roberts 1975) and Scotia (Christie 1975). The normalized data for Pd and Pt in Table 2 have been plotted on Figures 3 and 4, whereas Ir values are shown in Figure 5.

Samples of contact ore from Lunnon Shoot

Primary contact ore at Lunnon Shoot has been sampled from 13 different locations and summary results are recorded in Table 3a; full

### Table 2. Metal Values in Samples from Other Nickel Sulfide Deposits

<table>
<thead>
<tr>
<th>DEPOSIT</th>
<th>TYPE</th>
<th>EXP.</th>
<th>Ni</th>
<th>Cu</th>
<th>Co</th>
<th>S</th>
<th>Pt</th>
<th>Pd</th>
<th>Ir</th>
<th>Au</th>
<th>S:Ni</th>
<th>Ni:Cu</th>
<th>Ni:Co</th>
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</thead>
<tbody>
<tr>
<td>REDROSS</td>
<td>V</td>
<td>1</td>
<td>6.49**</td>
<td>0.58</td>
<td>0.14</td>
<td>15.81</td>
<td>979</td>
<td>117</td>
<td>62</td>
<td>2.45</td>
<td>11.18</td>
<td>45.6</td>
<td></td>
</tr>
<tr>
<td>NEPEAN</td>
<td>V</td>
<td>2</td>
<td>11.55</td>
<td>1.44</td>
<td>0.13</td>
<td>18.6</td>
<td>1896</td>
<td>225</td>
<td>80</td>
<td>1.61</td>
<td>8.0</td>
<td>89.6</td>
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</tr>
<tr>
<td>FORREASTINIA</td>
<td>D</td>
<td>3</td>
<td>3.31</td>
<td>0.16</td>
<td>5.08</td>
<td>470</td>
<td>72</td>
<td>25</td>
<td>1.54</td>
<td>20.2</td>
<td>-</td>
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<tr>
<td>PERSEVERANCE</td>
<td>D</td>
<td>4</td>
<td>2.19</td>
<td>0.10</td>
<td>7.75</td>
<td>293</td>
<td>34</td>
<td>34</td>
<td>3.54</td>
<td>21.9</td>
<td>-</td>
<td></td>
<td></td>
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<tr>
<td>SHANGANI</td>
<td>K</td>
<td>5</td>
<td>9.7</td>
<td>1.2</td>
<td>-</td>
<td>1300</td>
<td>2000</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>81.4</td>
<td>-</td>
<td>-</td>
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<tr>
<td>HITURA</td>
<td>K</td>
<td>6</td>
<td>1.96</td>
<td>0.25</td>
<td>-</td>
<td>11.6</td>
<td>180</td>
<td>182</td>
<td>-</td>
<td>-</td>
<td>7.04</td>
<td>-</td>
<td>-</td>
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<tr>
<td>SCOTIA</td>
<td>T</td>
<td>7</td>
<td>1.5</td>
<td>1.3</td>
<td>-</td>
<td>346</td>
<td>364</td>
<td>11</td>
<td>123</td>
<td>-</td>
<td>1.1</td>
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<td>-</td>
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<tr>
<td>NORT'U'K</td>
<td>T</td>
<td>8</td>
<td>1.13</td>
<td>1.9</td>
<td>-</td>
<td>2300</td>
<td>7200</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.68</td>
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### Table 2b. Mean Values Recalculated to 100% Sulfides

<table>
<thead>
<tr>
<th>DEPOSIT</th>
<th>Ni</th>
<th>Cu</th>
<th>Co</th>
<th>S</th>
<th>Pt</th>
<th>Pd</th>
<th>Ir</th>
<th>Au</th>
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<tbody>
<tr>
<td>REDROSS</td>
<td>14.70</td>
<td>1.32</td>
<td>0.31</td>
<td>38.93</td>
<td>-</td>
<td>1951</td>
<td>299</td>
<td>213</td>
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<tr>
<td>NEPEAN</td>
<td>22.60</td>
<td>2.83</td>
<td>0.27</td>
<td>36.77</td>
<td>-</td>
<td>3741</td>
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<td>156</td>
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<tr>
<td>FORREASTINIA</td>
<td>24.50</td>
<td>1.21</td>
<td>37.57</td>
<td>-</td>
<td>3479</td>
<td>534</td>
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<tr>
<td>PERSEVERANCE</td>
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<td>0.48</td>
<td>38.90</td>
<td>-</td>
<td>1469</td>
<td>148</td>
<td>172</td>
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<tr>
<td>SHANGANI</td>
<td>9.7</td>
<td>1.2</td>
<td>38.90</td>
<td>-</td>
<td>1300</td>
<td>2000</td>
<td>-</td>
<td>100</td>
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<tr>
<td>HITURA</td>
<td>7.20</td>
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<td>-</td>
<td>661</td>
<td>668</td>
<td>-</td>
<td>-</td>
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<tr>
<td>SCOTIA</td>
<td>4.5</td>
<td>3.9</td>
<td>1038</td>
<td>98</td>
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<td>109</td>
<td>-</td>
<td>-</td>
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<tr>
<td>NORT'U'K</td>
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<td>47770</td>
<td>-</td>
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### Table 3a. Mean Values in Concentrates Recalculated to 100% Sulfides

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<tr>
<th>DEPOSIT</th>
<th>TYPE</th>
<th>EXP.</th>
<th>Ni</th>
<th>Cu</th>
<th>Co</th>
<th>S</th>
<th>Pt</th>
<th>Pd</th>
<th>Au</th>
<th>S:Ni</th>
<th>Ni:Cu</th>
<th>Ni:Co</th>
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<tr>
<td>WINDARRA</td>
<td>V</td>
<td>9</td>
<td>54144</td>
<td>14.84</td>
<td>1.36</td>
<td>0.32</td>
<td>43.89</td>
<td>1310</td>
<td>3280</td>
<td>901</td>
<td>3.96</td>
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<tr>
<td>SCOTIA</td>
<td>V</td>
<td>9</td>
<td>3206</td>
<td>23.07</td>
<td>1.45</td>
<td>0.26</td>
<td>35.65</td>
<td>1461</td>
<td>3110</td>
<td>1020</td>
<td>1.54</td>
<td>15.9</td>
</tr>
</tbody>
</table>

** Values for Ni, Cu, Co and S in wt% Pd, Pt, Ir and Au in ppb.

(1) Keays & Davison (1976), Delgarno (1975): weighted mean of 9 random core samples; recalcula"tion to 100% sulfides based on the mean S:Ni ratio. (2) Keays (in prep.): mean of 7 samples of drill core representing a drilled length of 3.75m of contact ore; weighted by core length and S content. Description of deposit by Sheppy & Rowe (1975) and Barrett et al. (1976). (3) Keays & Davison (1976): weighted mean of 8 samples of drill core; recalcula"tion to 100% sulfides based on the mean S:Ni ratio. (4) Keays & Davison (1976): mean of 2 hand specimens; recalcula"tion to 100% sulfides based on the mean S:Ni ratio. Description of deposit by Martin & Allchurch (1975). (5) Maldrett & Cabrill (1976): data for an unknown number of massive sulfides; assumed to be 100% sulfides, but probably contain"ing 90% on the basis of experience at Kambalda. Analytical methods: unknown. (6) Meikle et al. (1976): mean (unweighted) of 36 samples with the highest S content; recalcula"tion to 100% sulfides based on the S:Ni ratio. Analytical method: fire assay and emission spectrography. (7) Maldrett & Cabrill (1976): preferred data for overall average, including the composition of massive sulfides. Analytical method: unknown. (8) Sinnamon (1966): mean (unweighted) of 36 and 38 samples, respectively, including composition for massive sulfides (assumed to be 100% sulfides). Analytical method: unknown. (9) Weighted mean for samples of concentrate with recalcula"tion to 100% sulfides based on analysis of the silicate fraction. The anomalously high S content of the Windarra samples reflects the incorporation of sulfide-bearing sediments into ore during mining. Analyses by W.M.C.
Details are given in Keays et al. (in prep.). The results for these three sample categories have been normalized to 100% sulfides and recorded in Table 3b. Values for Pd are variable and range from 176-1232 ppb, yet all but three ore sections show the matrix layer to have higher values than the massive layer. Iridium values are more uniform; most fall between 100-300 ppb. The matrix layer contains less Ir than the massive layer in all but two sections. In the absence of better data, the mean of the combined values for the integrated samples and the core from KA 4-12, given in Table 3b(iv), has been taken to represent contact ore from Lunnøn Shoot; it is plotted in Figures 3 and 5 together with an envelope representing the spread of individual samples. The Au values in Table 3b vary over the range 11-730 ppb and broadly correlate with Cu; with one exception, sulfides in the matrix layer contain more Au than in the massive layer, usually by a factor of more than two.

The distribution of Pd, Ir and Au within the matrix and massive ore layers is fully discussed by Keays et al. (in prep.), and only data for the best sampled section (drill hole KA4-12) are plotted. Figure 6 shows the relative enrichment of the matrix layer in Pd, Au and Cu, and of the massive layer in Ir; it also shows that the distribution of Pd and Ir within ore layers is not uniform.

Samples of sulfide stringers from Lunnøn Shoot

Stringers of primary sulfide within the footwall basalt have been sampled in drill hole KA 4–12 (three separate stringers), and beneath the massive layer in the 505 stope (one stringer). Sulfide stringers in a quartz vein overlying the massive layer, sampled in the 605 stope, were also analyzed. When results are normalized to 100% sulfides (Keays et al., in prep.), they show that four stringers have anomalously high values for Pd (1400–1760 ppb) and Au (857–2520 ppb), and four are relatively enriched in Cu. All five are enriched in Pd, Au and Cu relative to the adjacent massive ore. The level of Ir seems normal and is usually comparable to normalized values in adjacent massive ore. Keays & Crocket (1970) also found that footwall stringers below the main orebodies at Sudbury were enriched in the precious metals although their Ir contents commonly were low.

Sulfide mineral separates

Separates of individual sulfide phases (pentlandite, pyrrhotite, pyrite and chalcopyrite) were obtained from samples of primary massive ore from Lunnøn, Juan, Long and Durkin Shoots (Fig. 2) and analyzed for Pd, Ir and Au. The results demonstrate that pentlandite is the principal host for Pd, that Ir is almost uniformly distributed between all sulfide phases, and that pyrite and chalcopyrite are the principal hosts for Au (Keays et al., in prep.).

Precious Metals in the Ultramafic Host Rocks

The ultramafic host rocks have experienced varying degrees of metamorphism, serpenitization and talc-carbonate alteration, but detailed chemical studies at several deposits, e.g., Kambalda (Ross 1974, Ross & Hopkins 1975),
Nepean (Barrett et al. 1976), Windarra (Watchman 1971, Santul 1975), Mount Edwards (Hough 1976), and Scotia (Nesbitt 1971, Simon 1972) suggest that these processes have usually effected little change apart from the addition of H₂O and CO₂. When these chemical data are combined with the common preservation of original spinifex textures (representing the liquid-rich fraction) and cumulus textures they indicate that these rocks formed from high-Mg liquids (>20% MgO) containing varying proportions of forsteritic olivine (>Fo₉₀). At Lunnon Shoot there is strong evidence that the ultramafic sequence formed from varying mixtures of a liquid containing about 20–24% MgO and crystals of about Fo₉₀ olivine (Ross 1974). Subsequent studies indicate that these two components could account for the range of compositions and textures encountered around the Kambalda Dome, and, in particular, the compositions of the meta-olivine peridotites directly overlying contact ore zones. Available data for the other volcanic-type deposits in Western Australia favor similar components in the original magmas. This concept of a range of ultramafic compositions being formed by simple two-component systems (liquid + olivine) is supported by the occasional occurrence of relict igneous olivine (e.g., Kambalda, Scotia), and the experimental studies of Arndt (1976).

If these ultramafic rocks resulted from such mixtures, measurement of the abundances of precious metals in the original liquid and olivine should determine values in rocks resulting from mixtures of these components. Furthermore, if these measurements are combined with data for the sulfides they should indicate the distribution of precious metals between the silicate and sulfide melts. According, we have analyzed numerous samples of spinifex-textured ultramafic rock, believed to represent original crystal-free liquid, and three samples of relict olivine from the basal unit overlying Victor Shoot (Fig. 2).

As the metapicrites in Table 4 do not contain anomalous concentrations of sulfides, their precious-metal values should represent original highly magnesian liquids (plus or minus a few percent olivine) provided these metals have not been redistributed by postigneous processes.
(Although ore-associated units were not sampled, the sample locations range from between ore-associated units to well above ore-associated units; results show no systematic variation in precious-metal values with location). Some redistribution of Au has almost certainly occurred, but Pd and Ir are believed to have been essentially stable. Results for the seven sets of metapicrite samples show little variation in MgO, Pd and Ir values, with the exception of the anomalously high Ir result from Mount Clifford. Palladium values range from 7.40-11.60 ppb; there is no apparent difference between the first four results from ore-bearing environments and the remaining three. Iridium values are lower in the two barren environments and have resulted in higher Pd:Ir ratios, but the lower Ir value in the Ora Banda sample may relate to its lower MgO content (Keays et al., in prep.). The single Pt value, from Munro Township, represents only three samples from the A3 zone, as MacRae & Crocket (1977) suspect seawater leaching of Pt from the other three flow top samples.

Mean values for three mineral separates containing almost pure olivine and negligible sulfides (Table 4) indicate that original olivines were enriched in Ir and almost devoid of Pd and Au relative to material representing the original, coexisting high-Mg liquids.

**DISCUSSION**

**Precious metals in sulfide ores**

Although it is widely accepted that the sulfides in volcanic-type deposits are of magmatic origin, there is uncertainty about the extent to which original compositions have been modified during postigneous processes. Our view is that the coherence of the Ni:Cu and Ni:Co ratios shown in Figure 7 suggest that the sulfides have experienced very limited modification across the wide range of metamorphic settings and associated ultramafic-rock alteration assemblages (relict olivine, serpentine and talc-carbonate) repre-
TABLE 3b. METAL VALUES RECALCULATED TO 100% SULFIDES IN SAMPLES OF
CONTACT ORE FROM LUMNO CONTACT

<table>
<thead>
<tr>
<th>SAMPLE NO.</th>
<th>LOCATION</th>
<th>TKtracts</th>
<th>ORK TYPE</th>
<th>THICKNESS (metres)</th>
<th>Ni</th>
<th>Cu</th>
<th>S</th>
<th>Pd</th>
<th>Ir</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z10640</td>
<td>4 Level 1</td>
<td>Matrix</td>
<td>1.83</td>
<td>12.66± 2.36</td>
<td>38.00</td>
<td>1108</td>
<td>136</td>
<td>730</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z10639</td>
<td>403-405 2</td>
<td>Massive</td>
<td>0.46</td>
<td>5.11 ± 1.73</td>
<td>39.87</td>
<td>1232</td>
<td>255</td>
<td>552</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z10636</td>
<td>5 Level 3</td>
<td>Combined</td>
<td>2.29</td>
<td>9.92 ± 2.05</td>
<td>38.67</td>
<td>1153</td>
<td>179</td>
<td>665</td>
<td></td>
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</tr>
<tr>
<td>Z10635</td>
<td>&quot;</td>
<td>Massive</td>
<td>0.91</td>
<td>10.07 ± 0.02</td>
<td>38.83</td>
<td>321</td>
<td>168</td>
<td>10.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z10626</td>
<td>710 Stope</td>
<td>Combined</td>
<td>2.74</td>
<td>10.76 ± 0.41</td>
<td>38.83</td>
<td>287</td>
<td>114</td>
<td>39.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z10625</td>
<td>&quot;</td>
<td>Matrix</td>
<td>0.46</td>
<td>10.89 ± 1.15</td>
<td>38.83</td>
<td>251</td>
<td>196</td>
<td>164</td>
<td></td>
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</tr>
<tr>
<td>Z10628</td>
<td>704/8 Stope</td>
<td>Combined</td>
<td>2.59</td>
<td>11.25 ± 0.30</td>
<td>38.83</td>
<td>190</td>
<td>143</td>
<td>46.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z10627</td>
<td>&quot;</td>
<td>Massive</td>
<td>1.00</td>
<td>10.35 ± 0.65</td>
<td>38.83</td>
<td>271</td>
<td>326</td>
<td>111</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z10630</td>
<td>801 Stope</td>
<td>Massive</td>
<td>0.91</td>
<td>9.73 ± 0.19</td>
<td>38.83</td>
<td>264</td>
<td>220</td>
<td>41.1</td>
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<td></td>
</tr>
<tr>
<td>Z10629</td>
<td>&quot;</td>
<td>Combined</td>
<td>0.30</td>
<td>9.89 ± 0.06</td>
<td>38.83</td>
<td>296</td>
<td>279</td>
<td>43.6</td>
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<tr>
<td>Z10632</td>
<td>807 Stope</td>
<td>Massive</td>
<td>0.30</td>
<td>11.12 ± 0.10</td>
<td>38.83</td>
<td>799</td>
<td>252</td>
<td>70.2</td>
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<td></td>
</tr>
<tr>
<td>Z10631</td>
<td>&quot;</td>
<td>Combined</td>
<td>0.12</td>
<td>12.15 ± 0.60</td>
<td>38.83</td>
<td>950</td>
<td>219</td>
<td>121</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z10634</td>
<td>813 Stope</td>
<td>Massive</td>
<td>0.30</td>
<td>11.26 ± 0.40</td>
<td>38.83</td>
<td>883</td>
<td>255</td>
<td>605</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z10633</td>
<td>&quot;</td>
<td>Combined</td>
<td>1.52</td>
<td>10.49 ± 0.09</td>
<td>38.83</td>
<td>827</td>
<td>250</td>
<td>505</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z10638</td>
<td>827 Stope</td>
<td>Massive</td>
<td>1.22</td>
<td>9.77 ± 0.78</td>
<td>38.83</td>
<td>415</td>
<td>203</td>
<td>103</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z10637</td>
<td>&quot;</td>
<td>Combined</td>
<td>0.55</td>
<td>8.98 ± 1.01</td>
<td>38.83</td>
<td>212</td>
<td>239</td>
<td>68.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| (14) CORE SAMPLES |

| KM-12 4 Level 1 | Matrix | 4.24 | 9.45 ± 1.19 | 38.41 | 615 | 112 | 171 |
| KM-12 4 Level 4 | "       | 4.69 | 9.00 ± 0.58 | 38.83 | 257 | 173 | 70.9 |
| KM-13 5 Level 2 | Combination | 5.73 | 9.28 ± 0.96 | 38.83 | 475 | 135 | 132 |
| KM-13 5 Level 5 | "       | 3.57 | 10.88 ± 0.53 | 38.83 | 652 | 121 | 92.3 |
| KM-13 5 Level 5 | "       | 1.50 | 6.63 ± 0.17 | 38.83 | 277 | 193 | 15.0 |

| (15) LUMP SAMPLER |

| 4-8 Inc. 703 Stope 5 | Matrix | 10.29 | 0.71 | 38.83 | 3154 | 167 | 394 |
| 4-8 Inc. 801 Stope 5 | "       | 9.46 | 38.83 | 682 | 210 | 89.1 |
| 4-7 Inc. 605 Stope 5 | "       | 9.31 | 38.83 | 505 | 179 | 11.0 |
| 4-7 Inc. 605 Stope 5 | "       | 9.90 | 38.83 | 169 | 69.8 |

| (16) MEAN OF COMBINED DATA FROM (14) AND (15) |

| Combined | 10.22 | 0.76 | 38.75 | 612 | 208 | 211 |

* Values for Ni, Cu, and S in wt.%; Pd, Au and Ir in ppb. All recalculations are based on the weighted mean 38NiH for Lumno contact ore of 3.98± (Ross & Hopkins 1975), unless indicated otherwise. This ratio is equivalent to a S content of 38.62%.

(1) Recalculations based on 38.62% S because of the relatively high Pd and Cu values.

(2) Recalculations based on sulfide content estimated from Fe analysis because of the relatively low Ni value; the resultant S content is probably more realistic than that derived from the weighted mean 38NiH.

(3) Combined values have been calculated by weighing the matrix and massive ore values for both thickness and S content. (b) As for (3), except the values have been weighted for sulfide content, using the data of Evers & Hudson (1972). (5) Sampling may not be true representative of the ore sections and combined values have not been calculated.

These results encourage us to discuss the relationships between the abundance of precious metals and composition of sulfide ores in terms of original igneous associations.

Figure 3 shows good correlation between Pd and Ni in 100% sulfides in the eight mean values for cored ore given in Table 1. As each value represents numerous samples and large tonnages of ore, the correlation is viewed as a significant guide to the relationship over the range of at least 10-20% Ni in 100% sulfides. The important qualification is that these sulfides are associated with komatiitic ultramafic rocks for which the composition of the original liquid fraction was in the range 20-25% MgO. Values for core samples from Redross and Nepean and for concentrates from Scotia fall within the envelope and support the wider application of this relationship. The mean value for concentrates from Windarra is anomalously high, but it represents early mine production with a large component of supergene sulfides, and may reflect enrichment of Pd by weathering. Also included in Figure 3 are mean values for core samples from Forrestania and for two hand specimens of matrix ore from Perseverance; both points for these dunitic-type deposits lie very close to the regression line.

The relatively low position of the envelope for Lumno contact samples (Fig. 3) suggests that lump and chip sampling of ore zones will...
Ni in 100% sulfides. Symbols as for Fig. 3. The regression lines are for cored ore only with 
\( r = 0.92 \) for Ni:Co, and \( r = 0.77 \) for Ni:Cu.

give low values for Pd if they do not include 
the Pd-enriched footwall stringers. Although 
many of these stringers are included in ore 
production, most are included during mining of 
the thin, high-grade ore zones such as Durkin 
Shoot. The higher Pd value from Durkin Shoot 
suggest that the trend in Figure 3 may represent 
the minimum level of Pd in original sulfide 
melts.

The correlation between the Pt and Ni values 
in the representative samples of ore production 
is not good (Fig. 4, \( r = 0.53 \)). Individual samples show large variation in Pt relative to Ni, 
and although other Pt values recorded in Table 
2 fall within the envelope shown in Fig. 4 
(with the exception of Scotia), they effect little 
improvement on the correlation. Although the 
regression line of Figure 4 has been used in 
later calculations to estimate silicate-sulfide 
partitioning of Pt, we should not lose sight of 
the large measure of uncertainty in the relation-
ship between Pt and Ni. Because of this uncer-
tainty, and because Figures 3 and 4 show 
correspondence between the levels of Pd and Pt values, we have attempted to assess the re-
lationship between Pt and Ni on the basis of 
Pd:Pt ratios. These ratios, plotted against Ni 
in Figure 8, yield a correlation coefficient of 
0.66. The regression equation has been com-
bined with that for Pd versus Ni (Fig. 3) to 
derive an alternative expression for Pt versus Ni. 
This derived line of best fit is also shown in 
Figure 4. The correlation between Pd:Pt and 
Ni suggests a similar distribution of the two 
precious metals in ores and sulfide stringers.

Results for Ir in the volcanic-type deposits 
(Fig. 5) show the best correlation with Ni 
\( (r = 0.99) \), but it is only based on mean values 
for four samples: Scotia, Redross, Lunnon con-
tact, and the representative Kambalda Head 
sample. Use of the average value for Lunnon 
contact is justified because: (1) Ir is not en-
riched in footwall stringers, (2) it has a fairly 
uniform distribution in ore profiles when nor-
malized to 100% sulfides, and (3) the Lunnon 
contact sampling is adequately representative. 
Figure 5 also shows the mean values for core 
samples from Forrestania and two samples of 
matrix ore from the Perseverance deposit (Table 
2d), and both points for these dunitic-type 
deposits lie near the regression line.

The data for Au in these ores do not allow a 
meaningful discussion of its relationship with 
Ni. Apart from the discrepancy in Table 1 be-
tween the result of R.R. Keays (for Kambalda
Head) and those of WMC, referred to previously, the WMC values seem anomalously high in comparison with data given by Naldrett & Cabri (1976). Redistribution of Au is suggested by its substantial enrichment in sulfide stringers in Lunnon Shoot and also by the large variations between the ore layers at a given sampling site, and within an ore layer at different sampling sites, recorded by the data of Table 3 and Figure 6. Given the chemical mobility of Au and the alteration processes experienced by these volcanic-type deposits, e.g., hydrothermal alteration and leaching by seawater circulating through a hot, submarine volcanic pile, metamorphism, serpentinitization, and talc-carbonate alteration, it is probably unreasonable to expect that original igneous relationships can be fully assessed in the field. Anomalously high concentrations of Au in interflow sediments within the ultramafic sequence at Kambalda have been recently measured by Bavinton & Keays (1978); they suggested sea-floor leaching from the volcanic pile (but not necessarily from the sulfide ores) as a possible source.

The results presented in this paper illustrate the difficulties in sampling volcanic-type deposits to establish the average tenor of precious metals, particularly in instances where massive ore layers are present. For example, the Pd values in Figure 3 indicate that samples of large tonnages of ore production are suitable, whereas results from Lunnon Shoot show that close sampling of the matrix and massive layers is very likely to yield lower values for Pd. These lower values probably result from exclusion of the Pd-enriched sulfide stringers in the footwall. Figure 6 shows that the Pd content is different in each ore layer and that it also varies within ore layers at Lunnon Shoot. As we know that pentlandite is the major host for Pd (Keays et al., in prep.) and that the pentlandite content of the sulfides in the profile shown in Figure 6 is approximately constant, it is evident that the Pd content of the pentlandite increases substantially up the profile. If our results from Lunnon Shoot are representative, the average Pd content can only be properly assessed through sampling of ore production. There are fewer data available to guide comment on sampling for Pt, but the large variation shown by the envelope in Figure 4 suggests that only samples representing large tonnages of ore production should be considered. As the Pd:Pt ratio correlates more closely with Ni than does Pt, the distribution of Pt within ore zones and sulfide stringers may resemble that of Pd. Sampling for Ir appears to be much simpler for it has a more uniform distribution within the contact-ore zone at Lunnon Shoot and between sulfide phases, and it is not enriched in the sulfide stringers. However, the profile shown in Figure 6 points to differences between and within ore layers and suggests that composite samples across the entire ore zone are required. This study has not established any systematic patterns to the distribution of Au in the sulfides; other attempts to establish original relationships between Au and the composition of the sulfide fraction will probably be seriously inhibited by sampling difficulties. Our results suggest that mean values for Au will probably not exceed 500 ppb.

Precious metals in the ultramafic host rocks

The results for metapicrites given in Table 4

<table>
<thead>
<tr>
<th>Location</th>
<th>Po samples</th>
<th>McP</th>
<th>Pt</th>
<th>Pd</th>
<th>Ir</th>
<th>Au</th>
<th>Pd/Fe</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUNNON SHOOT</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td></td>
<td></td>
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<td>LUNNON SHOOT</td>
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<td>LUNNON SHOOT</td>
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<td>MOUNT CLIFFORD</td>
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<tr>
<td>MOUNT TOWNSHIP</td>
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<td>CRA BANDA</td>
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</tr>
</tbody>
</table>

* Nmc values in wt.%; precious metals in ppb. All results have been recalculated to volatile-free values. All analyses by R.R. Keays except for those in references 6, 9, and 10.

(a) METAPICRITES

(b) OXIDE REPEATES

(c) OTHER ROCKS

<table>
<thead>
<tr>
<th>Location</th>
<th>Po samples</th>
<th>McP</th>
<th>Pt</th>
<th>Pd</th>
<th>Ir</th>
<th>Au</th>
<th>Pd/Fe</th>
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<td>SEA FLOUR BASALT</td>
<td>11-13</td>
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<td>MOUNT ALBERT VICTOR</td>
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</tbody>
</table>

No. samples collected at heights ranging from 92-295 m above the basal contact; see Keays et al. (in prep.) for details. (5) Mean values for 6 samples collected at heights ranging from 6-270 m above the basal contact; see Keays et al. (in prep.) for details. (6) Sample from underground drill hole 5/35; FeO immediately air environment at the location 3 deposit (Andrews 1975). (7) Mean of 10 samples from the upper portion of a thin flow in drill hole 5/064 (Keays, in prep.). The relationship of the unit to mineralization lower in the succession is uncertain. (8) Mean of 6 samples from the A1 and A2 zones of the 6/071 flow units. The Pd value represents the mean of volumes 3, 4, 5 in Table 7 of Arndt et al. (1977) and the mean L.O.I. has been used to recalculate the results of Badger & Crocket (1977) to volatile-free values. The Pd values only represent the 3 samples from the A1 zone. (9) One sample (WMC No. 7 11539) of barren autoperlite distinct from known ore occurrences. (10) Mean of 3 analyses of separate containing >95% olivine (Fh98-88) and magnesil sulfides. (11) Crocket & Ochi (1977).
rocks from Munro Township in Ontario. The mean values of about 9–10 ppb Pd, 1.0–1.3 ppb Ir and 2–5 ppb Au are much higher than published values for sea-floor basalts shown in Table 4, but they are comparable with results for peridotite and dunite from the Mount Albert pluton in Quebec. Samples from barren environments seem to contain less Ir, but as the lower value in the Ora Banda sample may result from its lower MgO content, the significance of the lower average value for Munro samples must be questioned. There is no simple explanation for the anomalous levels of Ir in the 10 samples from Mount Clifford; the higher values are consistent and seem to be an original feature of the flow unit.

The high Ir and low Pd values in the olivine separate samples are consistent with results for MgO-rich, sulfide-free samples from Forrestania reported by Keays & Davison (1976, Fig. 7). Results given in Table 4 indicate Nernst partition coefficients \( D \) for the distribution of Ir, Pd and Au between olivine and coexisting high-Mg liquid \( (D = \text{ppb metal in olivine/ppb metal in silicate melt}) \) of approximately 4.7 for Ir, 0.02 for Pd, and 0.06 for Au, providing that equilibrium was attained. In view of the high temperatures required for the liquid (>1500°C: Arndt 1976) equilibrium relationships are considered most likely.

**Silicate–sulfide partitioning of precious metals**

If we assume the conventional view that sulfide concentrations have formed by segregation and accumulation of immiscible sulfide droplets from the host silicate magma, then it follows, as indicated by Rajamani & Naldrett (1978), that their composition will be governed by the composition of the host magma and the partitioning functions for the distribution of metals between the sulfide and silicate liquids. In the case of Ni and Cu, Naldrett & Cabri (1976) and Rajamani & Naldrett (1978) have showed a trend of decreasing Cu/(Cu+Ni) with increasing host-rock MgO for deposits of tholeiitic and komatiitic association. However, although their observations are true in a general sense they have simplified the actual relationships in volcanic-type deposits. Figure 7 shows that at Kambalda a range of Ni, Cu and Co values in sulfides coexisted with high-Mg liquid of essentially uniform composition containing variable proportions of olivine. Similarly, the results for Pd, Pt and Ir indicate a range of partition coefficients for these metals between a silicate melt of essentially constant composition and sulfide melts that span the range from <10 to >20% Ni. As the systematic variation in the content of precious and transition metals in the sulfides almost certainly precludes a metamorphic origin, we must consider other possibilities. For example, the variation could result from postsegregation re-equilibration with olivine during cooling, with different cooling rates giving rise to different nickel contents in the sulfide. However, the systematic increase of Pd and Cu with Ni (Figs. 3, 7) argues against olivine as a source of additional Ni, whereas an even more compelling argument against an olivine source is the observation that the Pd:Ir ratios in 100% sulfides with different Ni contents are essentially constant, and similar to the value measured in the Lunnon metapicrite. If we take the regression lines in Figures 3 and 5, at 10% Ni the Pd:Ir ratio is 6.37, and at 20% Ni it is 7.48; these ratios are very similar to the mean Pd:Ir value of 7.68 given in Table 4 for 10 samples of Lunnon metapicrite and strongly suggest that the high-Mg liquid was solely responsible for the composition of the coexisting sulfides.

A second source of this systematic variation could be the chemical environment of the coexisting silicate magma and sulfide melt prior to extrusion. Because Fe and Ni are the most important variables in the sulfides it is logical to look to factors that affect their partitioning between the two melts. Rajamani & Naldrett (1978) concluded that their partitioning will be largely influenced by factors that influence the activity coefficients of NiO and FeO in the silicate magma. They emphasized variation in components such as Al₂O₃, Na₂O, K₂O and CaO, but we seem to be dealing with only minor variation in the silicate components; we must look to other factors, such as \( f(O_2) \) and \( f(S_2) \). If each contact ore shoot and overlying ultramafic rocks originated from a separate magma pulse with a different path of ascent in the mantle, then each may have been exposed to different conditions. Small variations in the content of H₂O could lead to significant variations in \( f(O_2) \), which in turn are likely to influence the partitioning of Fe³⁺ between the silicate and sulfide melts. For example, higher values of \( f(O_2) \) should favor the partitioning of Ni²⁺ into the sulfide melt at the expense of Fe³⁺, and lead to lower \( S/\text{Ni} \) ratios. Similarly, variations in \( f(S_2) \) are likely to exert a differential influence on the partitioning of Ni²⁺ and Fe²⁺. We have also considered the possibility that differences in composition of the sulfide fraction resulted from varying departures from equilibrium, but in view of the high tempera-
tutes that must have prevailed, and the short equilibration times observed in experimental studies (Rajamani & Naldrett 1978, Clark & Naldrett 1972), we consider this an unlikely alternative. The relative proportion of sulfide to silicate melt may also be a contributing factor. For a given amount of silicate magma there may be a fixed budget of Ni, Cu, Co, Pt, Pd, Ir and Au entering the sulfide melt. Increasing amounts of S simply add more Fe from the silicate melt which in turn dilutes the concentration of the other metals. Another factor could be the timing of the separation of the sulfide melt from the silicate magma; melts that separated early would be enriched in all these metals relative to Fe whereas later melts, perhaps forming after the removal of small amounts of such early melts, would be enriched in Fe.

The small variation in the Pd:Ir ratios of ore sulfides noted above probably reflects very similar partition coefficients. To show this similarity, the Nernst partition coefficient, $D$ (where $D = \text{wt.}\%\text{ metal in sulfide liquid/\text{wt.}\%\text{ metal in silicate liquid}$) has been calculated for the range of 100\% sulfide compositions. The values for Pd and Ir in the Lunnon metapicrite (Table 4) and the value for Pt in the Munro Township samples have been used to represent the silicate melt, whereas the sulfide melt has been represented by values taken from the regression lines in Figures 3, 4 and 5. These calculations assume equilibrium relationships for sulfide-silicate partitioning of these elements; the results are plotted in Figure 9, together with $D$ values for Ni, Cu and Co calculated from the data of Ross (1974). Space does not permit a full discussion of all data in Figure 9, but it is interesting to note that the relative position of $D$ values for Cu and Ni are consistent with those observed by Rajamani & Naldrett (1978) in experimental charges containing 13.5\% MgO. Although the values for Pd and Pt exceed the estimate of Naldrett & Cabri (1976) for a single sulfide melt composition, there is broad agreement and the relative values are the same.

The data of Figure 9 provide a convenient reference for discussion of the relationships between Cu/(Cu+Ni) and Pt/(Pt+Pd) in nickel sulfide deposits of komatiitic and tholeiitic association. The results of Naldrett & Cabri (1976) are shown in Figure 10 together with results from this study. From inspection of the Ni:Cu ratios in Figure 7 and the relative position of the $D$ values for Pd and Pt in Figure 9, it is evident that komatiitic deposits should define a steep positive trend at very low Cu/(Cu+Ni) values, as is the case in Figure 10. Moreover, it is to be expected that there will be a family of similar trends, displaced to higher Cu/(Cu+Ni) values with decreasing MgO in the silicate liquid, and to lower Cu/
The anomalous Ir values in samples of meta-picrite from Mount Clifford suggest that some sulfide melts could have coexisted with anomalous silicate melts and thus would show departures from the trends presented here. In addition it should be noted that: (1) the Pt values in the carted ore samples of Table 1 may represent minimum values, (2) the correlation between Ni and Pt in sulfides is not good, and (3) the correlation between Ni and Ir is only based on a small sample population. The anomalously high values for Pd and Pt in samples from Durkin Shoot coincide with high Ir values calculated from data for mineral separates (Keays et al., in prep.) and indicate that significant departures from the trends may occur even amongst ore shoots associated with a single ultramafic sequence.

An enigmatic feature of the results for meta-picrites (Table 4) is the lack of obvious difference between values in samples from ore-bearing and barren areas. If the volume of sulfide melt was large relative to the volume of silicate melt we would expect some evidence of scavenging of metals from the latter. However, if the sulfide melt was enriched in precious and transition metals before the silicate and sulfide melt came into contact it could have enriched the high-Mg liquid. Obviously the unknowns preclude firm deductions, but the similarity of silicate values favors the possibility that the volume of sulfide melt was small in relation to that of high-Mg liquid.

The results for olivine (Table 4) enable us to make some general comments on the distribution of precious metals in deposits associated with original silicate liquids of higher and lower MgO content. Liquids containing more than, say, 25% MgO can only be formed from melting of residual olivine in the source diapir (Arndt 1977). If the precious-metal content of this olivine is similar to that of relict olivine at Kambalda, the resulting silicate liquid will contain more Ir, less Pd and probably less Au than the Lunnon metapicrite. The lower Pt values obtained by MacRae & Crocket (1977) in more olivine-rich sections of units suggest that Pt will also decrease as MgO increases. These differences should be reflected in lower Pd:Ir values in coexisting sulfide melts, but they are likely to be small; not surprisingly, values for the Perseverance and Forrestania deposits (believed to be associated with original silicate liquids containing more than 25% MgO) plot close to the regression lines in Figures 3 and 5. Conversely, liquids containing less than about 20% MgO should contain less Ir, more Pd, Au,
and probably more Pt than the Lunnon metamorphic and result in higher Pd:Ir ratios in coexisting sulfide melts.

**Summary and Conclusions**

We have studied the distribution of precious metals in the sulfides and associated host rocks of volcanic-type nickel sulfide deposits in Western Australia. Although the high-Mg liquid fraction of the komatiitic host rocks appears usually to have been restricted to the range of 20–25% MgO, we have observed compositions for the associated massive and matrix sulfides that span the range of 10–23% Ni in 100% sulfides. The level of Pd, Pt and Ir in these sulfides increases with increasing Ni, whereas Au values are more erratic. Sampling of numerous ore sections and footwall sulfide stringers from the contact-ore zone at Lunnon Shoot has shown that Pd is commonly depleted from the massive ore layer and enriched in the footwall stringers together with Cu and Au; we conclude that the only reliable method to accurately establish original Pd values is to sample large tonnages of mine production. A similar conclusion probably applies to Pt. The distribution of Ir is much more uniform and close sampling of complete ore sections should provide a representative sample. Individual ore samples are inadequate measures of the abundance of Pd, Ir and Au, because their concentration in sulfides varies within ore layers and within individual sulfide minerals.

Analyses of numerous samples of metamorphic, believed to represent the high-Mg liquid fraction of the associated ultramafic rocks, show similar Pd and Ir values in ore-bearing and barren environments, with Pd:Ir ratios common in the range of 6–10. Almost pure separates of relict olivine from Kambalda are enriched in Ir and impoverished in Pd and Au relative to the material representing the original coexisting liquid. These results have allowed us to calculate Nernst partitioning coefficients for the coexisting silicate and sulfide melts over the range of 10–20% Ni in sulfides. We find very similar D values for Pd and Ir over this range (138–319 for Pd, 167–327 for Ir), and much lower values for Pt (73–120). The Pd:Ir ratio of the sulfides ranges from 6.37 at 10% Ni to 7.49 at 20% Ni, and closely approximates that measured in the Lunnon metamorphic (7.68). This similarity indicates that precious-metal values in the sulfides reflect those in the associated high-Mg liquid, and that their systematic variation together with those observed for Ni, Cu and Co has resulted from the influence of factors other than bulk composition on the partitioning of metals between coexisting silicate and sulfide liquids.

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**References**


--- & DAVISON, R.M. (1976): Palladium, iridium, and gold in the ores and host rocks of nickel sulfide deposits in Western Australia. Econ. Geol. 71, 1214-1228.


KEELE, R.A. & NICKEL, E.H. (1974): The geology of a primary millerite-bearing sulphide assemblage and supergene alteration at the Otter Shoot, Kambalda, Western Australia. Econ. Geol. 69, 1102-1117.


pentlandite ore at Kambalda, Western Australia. 
_Econ. Geol._ 69, 93-107.


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