

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.

SOMMAIRE

Nous examinons les gisements nickelifères de type volcanique de l'Australie occidentale à deux points de vue: (1) relation entre composition globale des sulfures et teneurs en Pd, Pt, Ir et Au; (2) concentration de ces éléments dans des échantillons représentatifs de la fraction liquide et de l'olivine des séquences encaissantes ultramafiques

komatiitiques. Les analyses d'échantillons représentatifs, recalculées en posant la somme des sulfures égale à 100, montrent une corrélation positive variable entre les teneurs en métaux précieux et en Ni: bonne pour Ir, faible à modérée pour Pt, cette corrélation n'est pas établie pour Au. Notre étude de profils de minerai, venues de sulfures et concentrés nous a montré qu'il faut beaucoup d'efforts et de soins pour établir les teneurs moyennes en métaux précieux dans les gisements de type volcanique. Les échantillons de la fraction liquide riche en Mg qui coexistait avec les sulfures liquides originels donnent un rapport Pd:Ir semblable à celui des sulfures, ce qui indique que ce sont des liquides qui ont exercé l'influence prépondérante sur le partage relatif des métaux précieux entre liquides silicatés et sulfurés. Un large domaine de compositions de sulfures liquides a coexisté avec un domaine étroit pour les liquides silicatés; ce n'est pas la composition globale du liquide silicaté qui gouverne la composition du liquide sulfuré.

(Traduit par la Rédaction)

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

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(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 komatiitic 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

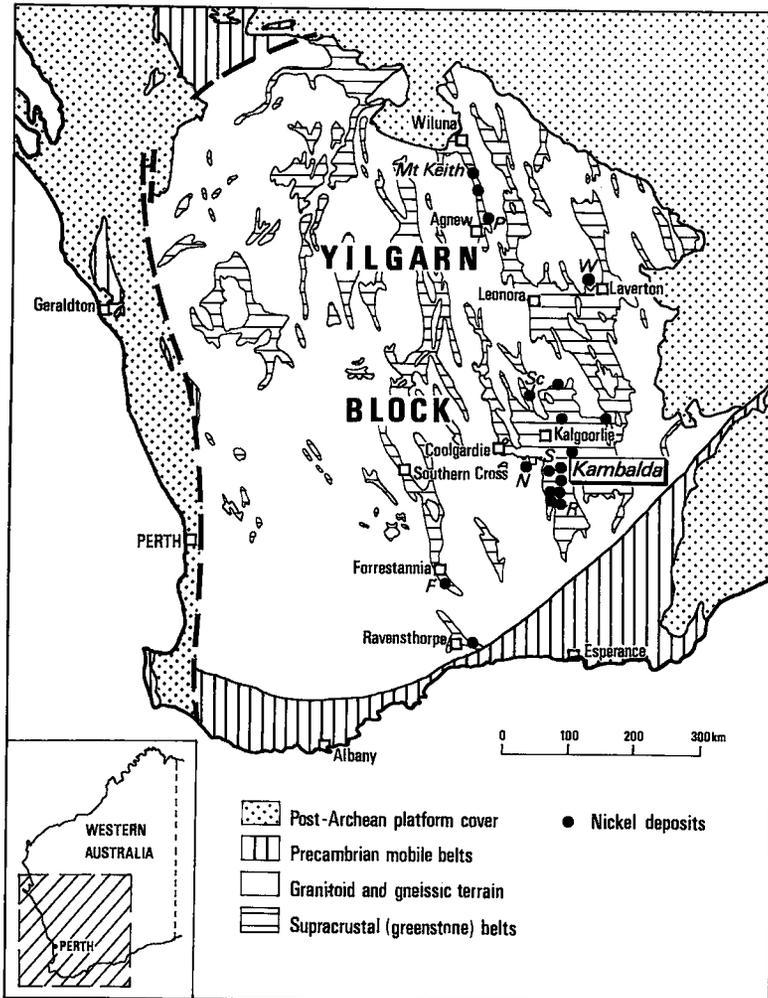


FIG. 1. Generalized geological map of the Yilgarn Block of Western Australia showing the greenstone belts and the location of the principal nickel sulfide deposits. Those mentioned in text include Kambalda, Forresteria (F), Nepean (N), Redross (R), Scotia (Sc), Spargoville (S), and Windarra (W).

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

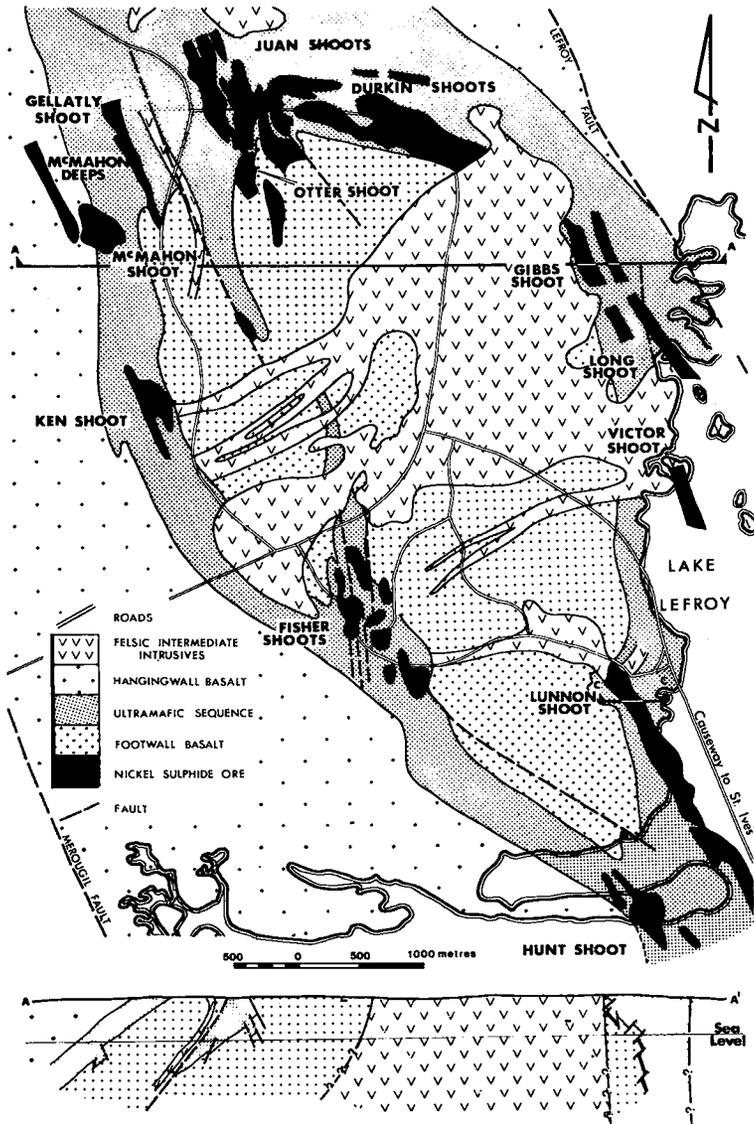


FIG. 2. Geological plan of the Kambalda Dome.

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 meta-olivine peridotite (commonly 34–45% MgO) which are in turn overlain by multiple thin units (< 10 m) of metapicrite and metaperidotite 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 1. METAL VALUES IN 18 COMPOSITE SAMPLES OF CARTED ORE FROM KAMBALDA AND NEPEAN, AND A KAMBALDA HEAD SAMPLE

(a) MEAN VALUES, WEIGHTED FOR TONNES

ORE SHOOT	ORE TONNES SAMPLED	Ni ¹	Cu	Co	S	Pt	Pd	Ir	Au	S:Ni	Ni:Cu	Ni:Co.
LUNNON	794,394 (0.175 ²)	2.40 (0.016)	0.20 (0.008)	0.06 (0.008)	7.73 (0.710)	284 (117)	318 (93.6)	- (150)	363 (150)	3.219	11.73	39.65
McMAHON	87,773 (0.302)	2.28 (0.026)	0.20 (0.005)	0.06 (0.005)	7.75 (1.242)	267 (128)	312 (134)	- (334)	356 (334)	3.391	11.45	38.06
FISHER	335,016 (0.243)	1.86 (0.025)	0.15 (0.007)	0.05 (0.007)	5.20 (0.737)	240 (113)	295 (83.1)	- (287)	340 (287)	2.791	12.05	40.36
JUAN	734,832 (0.342)	3.73 (0.022)	0.25 (0.010)	0.08 (0.010)	10.07 (1.147)	347 (204)	491 (114)	- (310)	348 (310)	2.697	14.77	48.29
KEN	149,727 (0.521)	3.55 (0.042)	0.28 (0.015)	0.08 (0.015)	10.49 (1.528)	277 (140)	458 (131)	- (193)	273 (193)	2.957	12.60	45.59
DURKIN	616,032 (0.312)	3.33 (0.017)	0.24 (0.008)	0.06 (0.008)	7.23 (0.662)	422 (193)	563 (132)	- (128)	312 (128)	2.170	13.89	53.15
NEPEAN	150,381 (0.499)	3.66 (0.033)	0.23 (0.010)	0.06 (0.010)	6.64 (0.940)	315 (132)	499 (109)	- (229)	293 (229)	1.817	15.69	59.58
KAMBALDA HEAD ³		3.25	0.22	0.06	8.88	-	363	59	113	2.734	14.44	50.19

(b) MEAN VALUES RECALCULATED TO 100% SULFIDES

ORE SHOOT	Ni	Cu	Co	S	Pt	Pd	Ir	Au
LUNNON	12.20 ⁴	1.04	0.31	39.27	1445	1615	-	1846
McMAHON	11.60 12.00 ⁵	1.05	0.31	40.69	1402	1636	-	1869
FISHER	13.95	1.16	0.34	38.94	1797	2213	-	2550
JUAN	14.40	0.97	0.30	38.84	1339	1894	-	1341
KEN	13.20 15.00 ⁵	1.19	0.33	44.35	1169	1937	-	1153
DURKIN	18.00	1.30	0.34	39.06	2277	3041	-	1686
NEPEAN	21.20	1.33	0.35	38.46	1824	2890	-	1697
KAMBALDA HEAD	14.20	.96	.26	38.80	-	1586	258	494

(1) Ni, Cu, Co, and S expressed in wt.%; Pd, Ir and Au in ppb. 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 Kenys & Davison (1976). (4) All values have been calculated from S:Ni ratios, except for the second set of data for McMahon & Ken (see #5). (5) Recalculation 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 mineralization within the lower third of the overlying ultramafic sequence. This *hanging-wall* mineralization 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* embraces 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 deposits 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 fraction 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 always dislocated by faulting. Where hanging-wall ore zones are present 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 associated with the millerite-bearing ores at Otter Shoot (Keele & Nickel 1974) and Gibbs Shoot, but as they have not been adequately sampled, the compositional range has been extended by the inclusion of material from the nickel-rich pentlandite-pyrrhotite ores at Nepean and Scotia (S:Ni values of about 1.8:1 and 1.6:1, respectively).

ANALYTICAL METHODS

Samples analyzed at the University of Melbourne were carefully cleaned and crushed in a soft iron mill known to have low precious-metal contents. Gold, Ir, Pd and Co were determined 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 $\pm 15\%$; 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 analyses (MgO) were obtained by XRF analysis following the method of Haukka & Thomas (1977).

Precious-metal determinations by Western Mining Corporation (WMC) follow the standard method for spectrographic analysis of ores, minerals and rocks by the fire-assay preconcentration technique (ASTM E400-71) described in the 1971 Annual Book of ASTM Standards; good comparative results were obtained with six other laboratories. Ni, Cu and Co were determined by AAS and routine precision is no less than $\pm 5\%$ for Ni and Cu and slightly higher for Co. Sulfur was measured by the barium sulfate gravimetric technique with a quoted accuracy of $\pm 3\%$.

PRECIOUS METALS IN NICKEL SULFIDE ORES

Four types of samples were obtained: representative samples of ore production, representative 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 approximately 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 tonnage-weighted means for the 18 samples from each shoot are recorded in Table 1a, together with data for a composite sample of ore production from all sources at Kambalda collected in 1973. Table 1b shows these values normalized 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 sulfide component of nickel sulfide ores to 100%

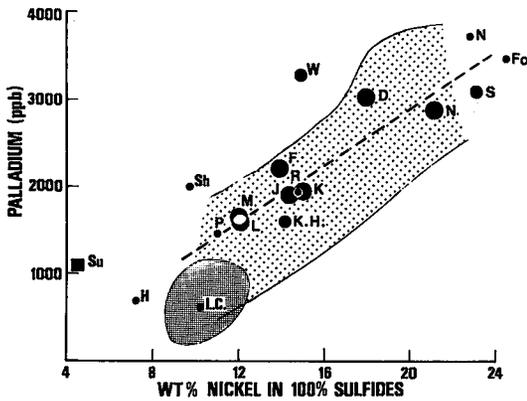


FIG. 3. Plot of Pd versus wt. % Ni in 100% sulfides. The large dots represent carted ore samples (Table 1), middle-sized dots represent concentrates (Table 2), and small dots represent core samples and hand specimens (Tables 2 and 3). Symbols are: D Durkin Shoot, F Fisher Shoot, Fo Forrestania, H Hitura, J Juan Shoot, K Ken Shoot, K.H. Kambalda Head, L Lunnon Shoot, L.C. Lunnon contact, M McMahan Shoot, N Nepean, P Perseverance, R Redross, S Scotia, Sh Shangani, Su Sudbury, W Windarra. The regression line ($r = 0.88$) is for carted ore samples only. Individual composite samples for Lunnon, Juan, Durkin and Nepean fall within the large shaded field. The smaller field represents individual samples of Lunnon contact ore.

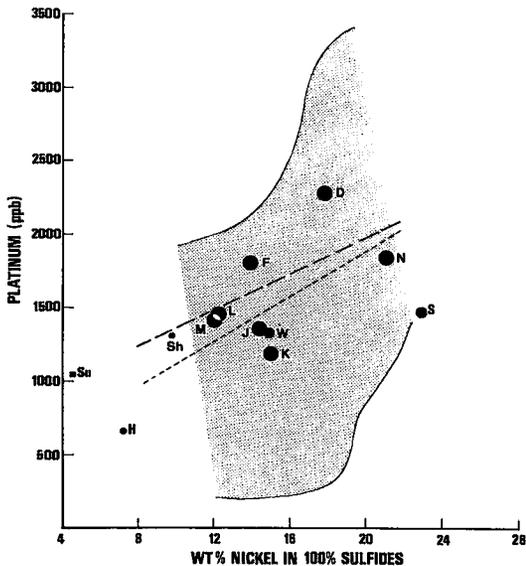


FIG. 4. Plot of Pt versus wt. % Ni in 100% sulfides. Symbols as for Fig. 3. Regression line ($r = 0.53$) is for carted ore samples only. The lighter line is the regression line derived from Pd:Pt ratios (see text); large shaded field as for Fig. 3.

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 Forrestania. 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

(a) MEAN VALUES													
DEPOSIT	TYPE	REF.	Ni	Cu	Co	S	Pt	Pd	Ir	Au	S:Ni	Ni:Cu	Ni:Co
REDROSS	V	1	6.49**	0.58	0.14	15.91	-	979	117	62	2.45	11.18	45.6
NEPEAN	V	2	11.55	1.44	0.13	18.6	-	1896	225	80	1.61	8.0	85.6
FORRESTANIA	D	3	3.31	0.16	-	5.08	-	470	72	25	1.54	20.2	-
PERSEVERANCE	D	4	2.19	0.10	-	7.75	-	293	30	34	3.54	21.9	-
SHANGANI	K	5	9.7	1.2	-	-	1300	2000	-	100	-	8.1	-
HITURA	K	6	1.96	0.25	-	11.6	180	182	-	-	-	7.84	-
SUDBURY	T	7	1.5	1.3	-	-	346	364	11	123	-	1.1	-
NORIL'SK	T	8	1.3	1.6	-	-	2600	6900	-	230	-	0.81	-
(picritic gabbro)													
NORIL'SK	T	8	1.13	1.9	-	-	2300	7200	-	290	-	0.68	-
(taxitic gabbro)													

(b) MEAN VALUES RECALCULATED TO 100% SULFIDES									
DEPOSIT		Ni	Cu	Co	S	Pt	Pd	Ir	Au
REDROSS		14.70	1.32	0.31	39.93	-	1951	299	213
NEPEAN		22.80	2.83	0.27	36.77	-	3741	443	158
FORRESTANIA		24.50	1.21	-	37.57	-	3479	534	188
PERSEVERANCE		11.00	0.48	-	38.90	-	1469	148	172
SHANGANI		9.7	1.2	-	-	1300	2000	-	100
HITURA		7.20	0.92	-	42.61	661	668	-	-
SUDBURY		4.5	3.9	-	-	1038	1092	33	369
NORIL'SK		9.0	10.8	-	-	18000	47770	-	1592
(picritic gabbro)									
NORIL'SK		7.6	10.9	-	-	13446	42092	-	1695
(taxitic gabbro)									

(c) MEAN VALUES IN CONCENTRATES RECALCULATED TO 100% SULFIDES													
DEPOSIT	TYPE	REF.	TONNES SAMPLED	Ni	Cu	Co	S	Pt	Pd	Au	S:Ni	Ni:Cu	Ni:Co
WINDARRA	V	9	54144	14.84	1.36	0.32	43.89	1310	3280	901	2.96	10.9	46.7
SCOTIA	V	9	3206	23.07	1.45	0.36	35.65	1461	3110	1020	1.54	15.9	63.1

* V volcanic; D dunitic; K komatiitic association; T tholeiitic association.

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

(1) Keays & Davison (1976), Dalgarno (1975): weighted mean of 5 random core samples; recalculation 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 3.57m 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; recalculation to 100% sulfides based on the mean S:Ni ratio. (4) Keays & Davison (1976): mean of 2 hand specimens; recalculation to 100% sulfides based on the mean S:Ni ratio. Description of deposit by Martin & Allchurch (1975). (5) Haldrett & Cabri (1976): data for an unknown number of massive sulfides; assumed to be 100% sulfides, but probably contain <9% on the basis of experience at Kambalda. Analytical method: unknown. (6) Hukli et al. (1976): mean (unweighted?) of 36 samples with the highest S content; recalculation to 100% sulfides based on the S:Ni ratio. Analytical method: fire assay and emission spectrography. (7) Haldrett & Cabri (1976): preferred data for overall average, including the composition of massive sulfides. Analytical method: unknown. (8) Smirnov (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 recalculation 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 Lunnon 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 Lunnon 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 Lunnon, 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, serpentinization and talc-carbonate alteration, but detailed chemical studies at several deposits, *e.g.*, Kamalda (Ross 1974, Ross & Hopkins 1975),

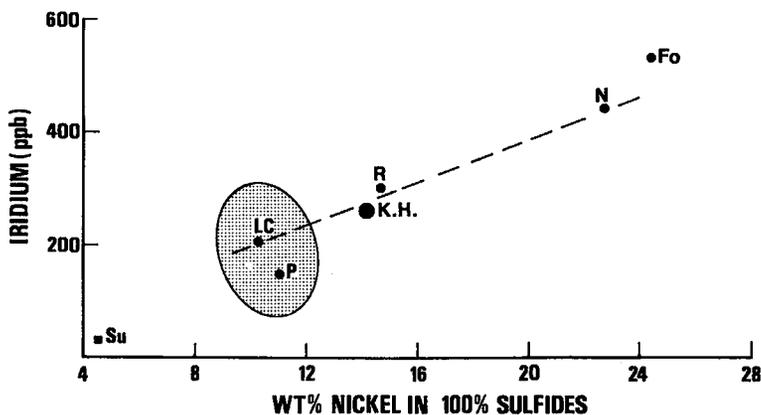


FIG. 5. Plot of Ir versus wt. % Ni in 100% sulfides. Symbols as for Fig. 3. Regression line ($r = 0.99$) is for L.C., K.H., R and N only. The shaded field represents individual samples of Lunnon contact ore.

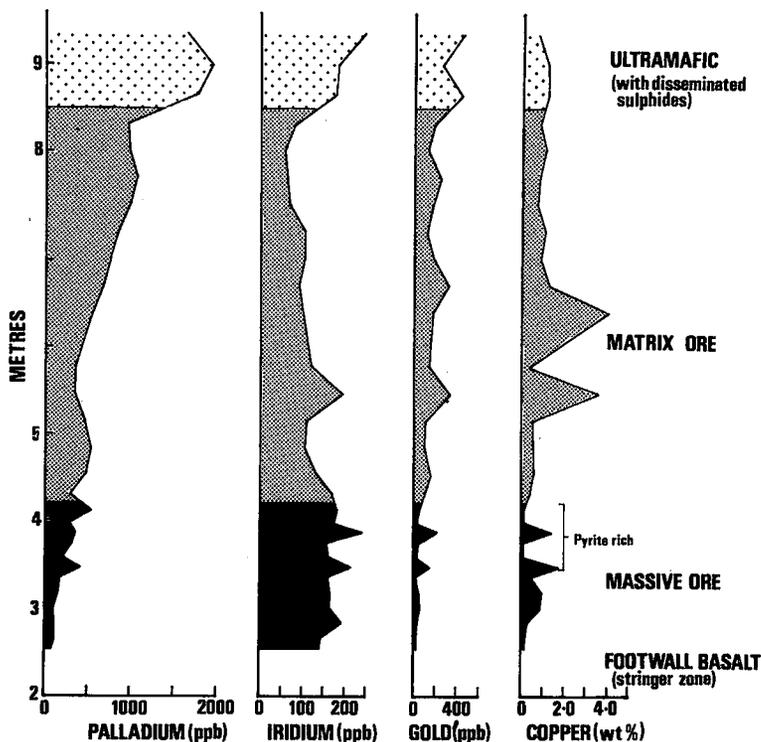


FIG. 6. Plot of Pd, Ir, Au and Cu in 100% sulfides for the contact ore zone in drill hole KA4-12 from Lunnon Shoot. Data from Keays & Davison (1976).

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 H_2O and CO_2 . 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 ($>Fo_{80}$). 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 Fo_{82} 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 ultra-

mafic 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.

TABLE 3a. METAL VALUES IN SAMPLES OF CONTACT ORE FROM LUNNON SHOOT

(i) INTEGRATED SAMPLES

SAMPLE NO.	LOCATION	REF.	ORE TYPE	THICKNESS (metres)							
					Ni	Cu	S	Pd	Ir	Au	Pd:Ir
Z10640	4 Level (403-405)	1	Matrix	1.83	5.13*	0.91	15.4	449	55.3	296	8.12
Z10639	"	1	Massive	0.46	4.46	1.51	34.8	1075	223	482	4.82
Z10636	5 Level	1	Matrix	1.83	4.85	0.38	16.4	106	16.3	28.7	6.50
Z10635	"	1	Massive	0.91	8.74	0.02	33.7	279	163	9.4	1.71
Z10626	710 Stope	1	Matrix	0.46	6.17	0.65	22.0	142	111	92.8	1.28
Z10625	"	1	Matrix	2.13	5.90	0.05	20.2	91.8	67.9	9.5	1.35
Z10628	704/8 Stope	1	Matrix	1.00	4.69	0.29	17.6	345	148	50.5	2.33
Z10627	"	1	Massive	1.00	8.68	0.17	34.4	464	263	93.6	1.76
Z10630	801 Stope	1	Matrix	0.91	5.49	0.11	21.9	149	124	23.2	1.20
Z10629	"	1	Massive	0.30	8.23	0.05	32.3	246	232	36.3	1.06
Z10632	807 Stope	1	Matrix	1.83	5.47	0.33	16.7	437	92.3	59.7	4.73
Z10631	"	1	Massive	0.30	8.50	0.08	29.0	611	193	53.7	3.16
Z10634	813 Stope	1	Matrix	1.22	5.31	0.19	18.3	416	120	285	3.47
Z10633	"	1	Massive	0.30	7.48	1.15	33.0	598	203	240	2.94
Z10638	827 Stope	1	Matrix	1.22	5.16	0.42	20.5	219	107	54.3	2.05
Z10637	"	1	Massive	0.55	8.0	0.90	34.6	189	213	43.0	0.89

(ii) CORE SAMPLES

KA4-12	4 Level	2	Matrix	4.24	5.04	0.64	20.53	312	62.3	91.5	5.60
"	"	2	Massive	1.49	8.16	0.50	36.51	217	158	56.2	1.37
KA4-13	"	3	Matrix	3.57	6.13	0.30	21.87	339	68	52	4.98
"	"	3	Massive	1.58	9.01	0.16	36.31	259	181	14	1.43

(iii) LUMP SAMPLES

4-8 inc.	703 Stope	4	Matrix		6.08	0.42	22.94	682	99	233	6.89
2,3	"	4	Massive		7.92		32.50	571	176	74.6	3.24
8-11 inc.	801 Stope	5	Matrix	2.02	5.15	0.92	19.42	594	46.3	51.2	12.83
4-7 inc.	"	5	Massive	1.05	7.78	0.45	32.45	422	150	9.2	2.81
1-7 inc.	605 Stope	6	Massive	1.0	8.46	0.50	33.19	310	144	59.7	2.15

* Values for Ni, Cu and S in wt.%; Pd, Ir and Au in ppb. All analyses by R. Keays except for Ni, Cu and S in (i) (by W.M.C.) and (ii) (from Ewers & Hudson 1972). (1) Each sample is a composite of chip samples across the ore layer. (2) Weighted averages (by sulfide content) for 14 samples of matrix ore and 16 samples of massive ore. (3) Weighted averages (by S content) for 3 samples of matrix ore and 7 samples of massive ore; KA4-13 was drilled adjacent to KA4-12. (4) Weighted averages (by S content) for 5 samples across the matrix sulfide layer and 2 samples from the massive sulfide layer. (5) Weighted averages (by S content) for 4 samples across the matrix layer and 4 samples across the massive layer. A gacitic porphyry forms the footwall to the massive layer. (6) Weighted average (by S content) of 8 samples across the massive layer; a quartz vein forms the hanging wall.

(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 re-distribution 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 A₂ 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 LUNNON SHOOT

(i) INTEGRATED SAMPLES

SAMPLE NO.	LOCATION	REF.	ORE TYPE	THICKNESS (metres)	Ni	Cu	S	Pd	Ir	Au
Z10640	4 Level	1	Matrix	1.83	12.66*	2.24	38.00	1108	136	730
Z10639	403-405	2	Massive	0.46	5.11	1.73	39.87	1232	255	552
		3	Combined	2.29	9.92	2.05	38.67	1153	179	665
Z10636	5 Level		Matrix	1.83	11.48	0.90	38.83	251	38.6	67.9
Z10635	"		Massive	0.91	10.07	0.02	38.83	321	188	10.8
			Combined	2.74	10.76	0.41	38.83	287	114	39.0
Z10626	710 Stope		Matrix	0.46	10.89	1.15	38.83	251	196	164
Z10625	"		Matrix	2.13	11.34	0.10	38.83	176	130	18.3
			Combined	2.59	11.25	0.30	38.83	190	143	46.0
Z10628	704/8 Stope		Matrix	1.00	10.35	0.65	38.83	761	326	111
Z10627	"		Massive	1.00	9.80	0.19	38.83	524	297	106
			Combined	2.00	9.99	0.34	38.83	604	307	108
Z10630	801 Stope		Matrix	0.91	9.73	0.19	38.83	264	220	41.1
Z10629	"		Massive	0.30	9.89	0.06	38.83	296	279	43.6
			Combined	1.21	9.78	0.15	38.83	274	239	41.9
Z10632	807 Stope		Matrix	1.83	12.45	0.75	38.00	994	210	136
Z10631	"		Massive	0.30	11.12	0.10	38.00	799	252	70.2
			Combined	2.13	12.15	0.60	38.00	950	219	121
Z10634	813 Stope		Matrix	1.22	11.26	0.40	38.83	883	255	605
Z10633	"		Massive	0.30	8.80	1.35	38.83	704	239	282
			Combined	1.52	10.49	0.69	38.83	827	250	505
Z10638	827 Stope		Matrix	1.22	9.77	0.79	38.83	415	203	103
Z10637	"		Massive	0.55	8.98	1.01	38.83	212	239	48.2
			Combined	1.77	9.43	0.88	38.83	327	218	79.3
(ii) CORE SAMPLES										
KA4-12	4 Level		Matrix	4.24	9.45	1.19	38.41	615	112	171
"	"		Massive	1.49	9.00	0.58	40.59	257	175	70.9
"	"	4	Combined	5.73	9.28	0.96	39.18	475	135	132
KA4-13	"	5	Matrix	3.57	10.88	0.53	38.83	602	121	92.3
"	"		Massive	1.58	9.63	0.17	38.83	277	193	15.0
(iii) LUMP SAMPLES										
4-8 inc.	703 Stope	5	Matrix		10.29	0.71	38.83	1154	167	394
2,3	"		Massive		9.46	-	38.83	682	210	89.1
8-11 inc.	801 Stope	5	Matrix		10.29	1.84	38.83	1188	92.6	102
4-7 inc.	"		Massive		9.31	0.54	38.83	505	179	11.0
1-7 inc.	605 Stope		Massive		9.90	0.58	38.83	363	169	69.8
(iv) MEAN OF COMBINED DATA FROM (i) AND (ii)										
		3,4	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 S:Ni for Lunnon contact ore of 3.982 (Ross & Hopkins 1975), unless indicated otherwise. This ratio is equivalent to a S content of 38.83%.

(1) Recalculation based on 38.0% S because of the relatively high Ni and Cu values.
 (2) Recalculation 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 S:Ni for Lunnon contact ore. (3) Combined values have been calculated by weighting the matrix and massive ore values for both thickness and S content. (4) As for (3), except the values have been weighted for sulfide content, using the data of Ewers & Hudson (1972). (5) Sampling may not be truly representative of the ore sections and combined values have not been calculated.

sented by the deposits plotted in Figure 7. 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 carted 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 be 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 Lunnon contact samples (Fig. 3) suggests that lump and chip sampling of ore zones will

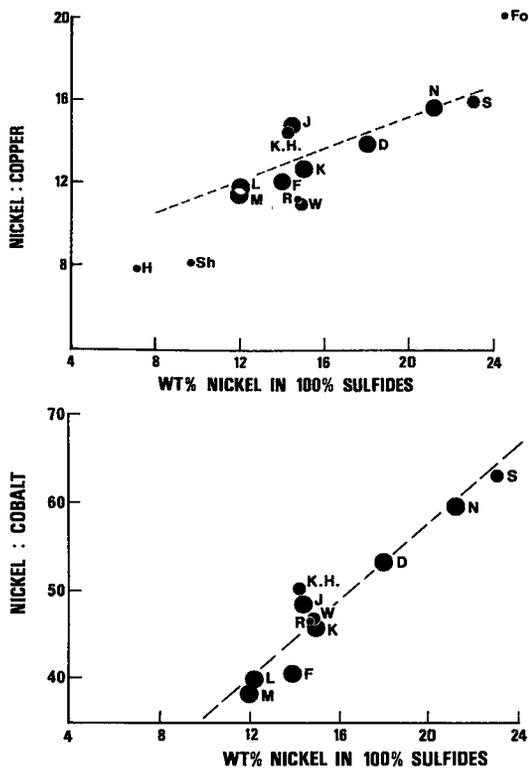


FIG. 7. Plot of Ni:Cu and Ni:Co versus wt. % Ni in 100% sulfides. Symbols as for Fig. 3. The regression lines are for carted ore only with $r = 0.92$ for Ni:Co, and $r = 0.77$ for Ni:Cu.

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

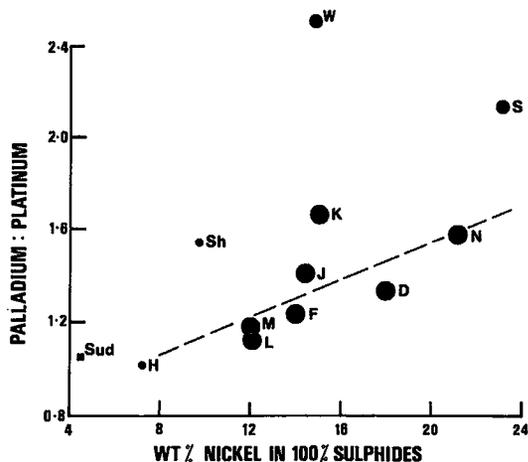


FIG. 8. Plot of Pd:Pt versus wt. % Ni in 100% sulfides ($r = 0.66$). Symbols as for Fig. 3.

the large measure of uncertainty in the relationship between Pt and Ni. Because of this uncertainty, and because Figures 3 and 4 show correspondence between the levels of Pd and Pt values, we have attempted to assess the relationship 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 combined 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 contact, and the representative Kambalda Head sample. Use of the average value for Lunnon contact is justified because: (1) Ir is not enriched in footwall stringers, (2) it has a fairly uniform distribution in ore profiles when normalized 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 between 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, serpentinization, 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 4. PRECIOUS METALS IN METAPICRITES AND OLIVINE

(a) METAPICRITES								
Location	No. samples	MgO	Pt	Pd	Ir	Au	Pd:Ir	Reference
LUNNON SHOOT (near ore)	10	23.10*	-	9.11	1.18	3.10	7.68	1
LUNNON SHOOT (near ore)	4	23.55	-	10.77	1.36	4.01	7.84	2
LONG SHOOT (near ore)	6	24.20	-	7.40	1.25	5.30	5.90	3
SPARGOVILLE (near ore)	1	22.12	-	11.60	1.29	0.17	9.35	4
MOUNT CLIFFORD (near ore?)	10	25.64	-	9.61	2.87	0.92	3.35	5
MUNRO TOWNSHIP (distant from ore)	6	25.6	15.1	10.4	1.0	1.9	10.3	6
ORA BANDA (distant from ore)	1	19.38	-	10.78	0.83	1.61	12.99	7
(b) OLIVINE SEPARATES								
VICTOR SHOOT (basal unit in drill hole KD 6042)	3	-	-	0.21	5.68	0.25	0.04	8
(c) OTHER ROCKS								
SEA FLOOR BASALT	11-13	-	-	<0.7	<0.02	2.8	-	9
MOUNT ALBERT PLUTON	5	-	-	7.9	2.4	1.1	3.3	10

* MgO 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.

(1) Mean values for 10 samples of the Lunnon metapicrite (Rose & Hopkins, 1975) from drill hole KD 127. (2) Mean values for 4 samples collected at heights ranging from 90-235 m above the basal contact; see Keays *et al.* (in prep.) for details. (3) 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. (4) Sample from underground drill hole 4/33 from immediate ore environment at the Location 3 deposit (Andrews 1975). (5) Mean of 10 samples from the upper portion of a thin flow in drill hole MCD 478 (Keays, in prep.). The relationship of the unit to mineralization lower in the succession is uncertain. (6) Mean of 6 samples from the A₁ and A₂ zones of 2 flow units. The MgO value represents the mean of columns 3, 4 and 5 in Table 7 of Arndt *et al.* (1977) and the mean L.O.I. has been used to recalculate the results of Macrae & Crocket (1977) to volatile-free values. The Pt values only represent the 3 samples from the A₂ zone. (7) One sample (WMC No. Z 11232) of barren metapicrite distant from known ore occurrences. (8) Mean of 3 analyses of separates containing >95% olivine (Fogg-93) and negligible sulfides. (9) Crocket & Teruta (1977). (10) Crocket & Chy (1972).

indicate that the liquid fraction of these komatiitic ultramafic rocks from the Eastern Goldfields of Western Australia contained values for Pd, Ir and Au similar to those in almost identical

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 ($>1500^\circ\text{C}$: 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 $\text{Cu}/(\text{Cu}+\text{Ni})$ 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 Al_2O_3 , Na_2O , K_2O and CaO , but we seem to be dealing with only minor variation in the silicate components; we must look to other factors, such as $f(\text{O}_2)$ and $f(\text{S}_2)$. 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 H_2O could lead to significant variations in $f(\text{O}_2)$, which in turn are likely to influence the partitioning of Fe^{2+} between the silicate and sulfide melts. For example, higher values of $f(\text{O}_2)$ should favor the partitioning of Ni^{2+} into the sulfide melt at the expense of Fe^{2+} , and lead to lower S:Ni ratios. Similarly, variations in $f(\text{S}_2)$ are likely to exert a differential influence on the partitioning of Ni^{2+} and Fe^{2+} . 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-

tures 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 $D = \text{wt. \% metal in sulfide liquid} / \text{wt. \% metal in silicate liquid}$) 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 re-

gression 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 $\text{Cu}/(\text{Cu}+\text{Ni})$ and $\text{Pt}/(\text{Pt}+\text{Pd})$ 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 $\text{Cu}/(\text{Cu}+\text{Ni})$ 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 $\text{Cu}/(\text{Cu}+\text{Ni})$ values with decreasing MgO in the silicate liquid, and to lower $\text{Cu}/$

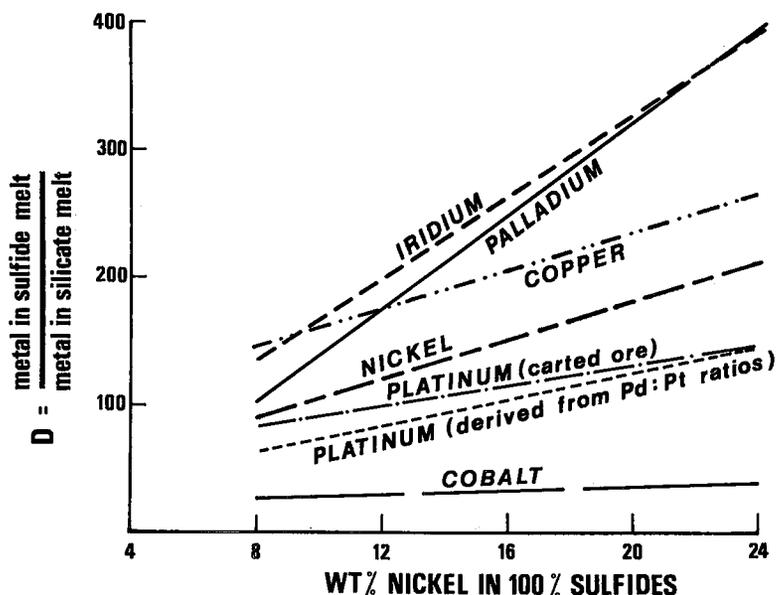


FIG. 9. Plot of Nernst partitioning coefficients (D) versus wt. % Ni in 100% sulfides.

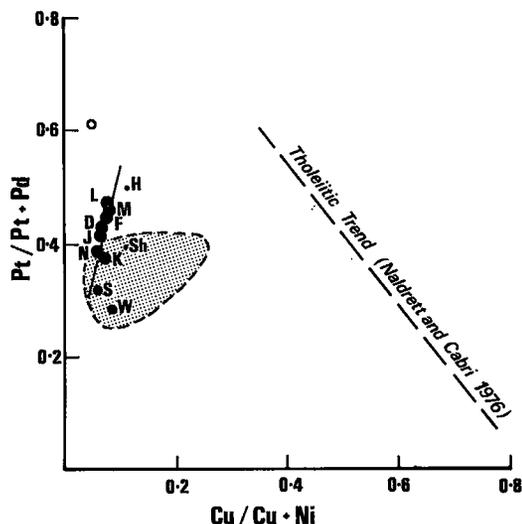


FIG. 10. Variation in Pt/Pt+Pd ratios as a function of the Cu/Cu+Ni ratios of nickel sulfide ore deposits. Symbols as in Fig. 3. The stippled area shows the komatiitic field defined by Naldrett & Cabri (1976). The open circle represents the Lunnon metapicrite, assuming the Pt value from the Munro Township samples (Table 4).

(Cu+Ni) values with increasing MgO. The komatiitic field defined by Naldrett & Cabri may be composite, whereas the trend defined in this study represents a very limited range of MgO in the original high-Mg liquid. As the komatiitic trends in Figure 10 represent a decrease in Pt/(Pt+Pd) with increasing MgO (decreasing Cu/(Cu+Ni)), the tholeiitic trend of Naldrett & Cabri (1976) shown in Figure 10 requires an increase in this ratio with increasing MgO. This requirement is better envisaged as a change in the relative position of the trends for Pd and Pt in Figure 9 from divergence with increasing Ni (decreasing Cu/(Cu+Ni)) to convergence.

Data presented in this paper indicate consistent variations in the partitioning of precious metals between host silicate liquids and the coexisting sulfide liquids which formed the volcanic-type deposits, but these results should be applied with caution. For example, although they may have general application to volcanic-type deposits the results can only be applied *sensu stricto* to nickel sulfide deposits associated with original ultramafic magmas having a high-Mg liquid fraction containing 20–25% MgO. Fortunately, this range includes most, and possibly all, volcanic-type deposits in Western Australia.

The anomalous Ir values in samples of metapicrite 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 Pd 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 metapicrites (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 & Crockett (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 metapicrite, 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 metapicrite, 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 commonly 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 metapicrite (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.

ACKNOWLEDGEMENTS

This study has been made possible by the financial support of the Australian Research Grants Commission, the Australian Institute of Nuclear Science and Engineering, and Western Mining Corporation Ltd. It has benefited considerably from the broader support of WMC; we are also grateful for their permission to publish. We have benefited from the contribution of many colleagues and warmly acknowledge their interest and help. Several geologists at Kambalda helped with sample collection, in particular Dr. P. Woolrich and Mr. R. Watchorn, whereas Mr. G.A. Travis provided both samples and stimulating comment during the course of the project. The analytical work at the University of Melbourne was assisted by Ms. R.M. Davison, and Messrs. P.J. McGoldrick and P. Hannaker. Dr. C.E. Gee carried out the statistical treatment of data and helped introduce much of the valuable WMC data to the project. Completion of the study has been assisted by a Visiting Fellowship (J.R.R.) at the Research School of Earth Sciences, A.N.U.; that support, and the help of Mr. R. Rudowski who separated the olivine samples, is gladly acknowledged. Mr. O.A. Bavinton offered many helpful comments, both during the project and on an earlier version of the manuscript. The final version has been improved by the comments of Dr. G. Loftus-Hills, Mr. J.J. Gresham and Dr. P. Woolrich at Kambalda, and the reviews of Professor J.H. Crockett and Dr. D.I. Groves.

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Received August 1978, revised manuscript accepted December 1978.