

GEOCHEMISTRY OF THE KAMBALDA IRON-NICKEL SULFIDES: IMPLICATIONS FOR MODELS OF SULFIDE-SILICATE PARTITIONING

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ABSTRACT

Geochemical data, from 72 sample profiles through eight Kambalda orebodies, indicate considerable variation in chemistry, both within and between orebodies. Within one orebody, matrix and disseminated sulfides are low in sulfur, compared to massive sulfides, and the Fe:Ni ratio is nearly constant. Between orebodies, however, this ratio markedly varies with Ni-tenor (Ni in 100% sulfides) ranging from 8 to 22%. The contrast in sulfur content between massive and matrix-disseminated sulfides is largely due to metamorphic alteration. Orebodies with contrasting Ni-tenors, however, are hosted by komatiites of similar composition and occur in identical tectonic and metamorphic settings; therefore, the Fe:Ni variability, which is common to all komatiite-hosted Ni deposits in Western Australia, is not related to metamorphic alteration. Variations in Fe:Ni ratio are attributed to variations in $f(\text{O}_2)$ in the sulfide-silicate system prior to eruption. Oxidation decreases the amount of Fe^{2+} available for partitioning to sulfide and polymerizes the melt, reducing the number of octahedral sites. Therefore, Ni, Cu and Co are the more strongly partitioned to sulfide. High-tenor ores are interpreted to be equilibrium compositions, whereas low- and medium-tenor ores are considered disequilibrium compositions inherited from equilibrium at depth.

Keywords: nickel sulfides, partition models, komatiites, oxygen fugacity, Kambalda, Australia.

SOMMAIRE

Les données géochimiques ont été recueillies au cours de 72 cheminements d'échantillonnage dans huit gisements de minéral, à Kambalda. Elles témoignent de variations chimiques considérables, tant dans un même gisement que d'un gisement à un autre. Dans le premier cas, les sulfures disséminés sont à basse teneur en S en comparaison des sulfures massifs, et le rapport Fe:Ni est quasiment constant. D'un gisement à l'autre, par contre, ce rapport varie fortement, la teneur en Ni (Ni dans sulfure à 100%) allant de 8 à 22%. Le contraste, au point de vue teneur en S, entre sulfures massifs et sulfures disséminés provient surtout de l'altération métamorphique. Les gisements à teneur en Ni fortement variable se trouvent dans des komatiites de compositions analogues et se présentent dans un même envi-

ronnement tectonique et métamorphique. Il s'en suit que la variabilité du rapport Fe:Ni, qui est commune à tous les gîtes de Ni dans komatiite en Australie occidentale, ne relève nullement de l'altération métamorphique. On attribue les variations du rapport Fe:Ni à celles de la fugacité $f(\text{O}_2)$ dans le système silicate-sulfure avant éruption. L'oxydation abaisse la quantité de Fe^{2+} disponible pour le partage avec les sulfures et elle polymérise le bain fondu, ce qui diminue le nombre de sites octaédriques. C'est pourquoi Ni, Cu et Co sont plus généreusement alloués au sulfure. On interprète les minerais à haute teneur comme compositions d'équilibre et ceux à basse ou moyenne teneur comme compositions de déséquilibre héritées d'un équilibre en profondeur.

(Traduit par la Rédaction)

Mots-clés: nickel (sulfure de), modèles de partage, komatiites, fugacité d'oxygène, Kambalda, Australie.

INTRODUCTION

Nickel sulfides were discovered at Kambalda, in Western Australia, by Western Mining Corporation in January 1966. The deposits were quickly developed, and production commenced in 1967 from the Lunnon shoot (Fig. 1). Kambalda is now one of the world's premier nickel-mining centres, contributing on average some 7% of the western world's annual production of nickel metal (Ross & Travis 1981). The Kambalda deposits are regarded as the type examples of komatiite-associated nickel deposits (Marston *et al.* 1981).

Kambalda ores may range from 8 to 22% Ni in 100% sulfides. This compositional variability has been widely recognized (Barrett *et al.* 1977, Woolrich & Giorgetta 1978, Ross & Keays 1979, Woolrich *et al.* 1981, Keays *et al.* 1981), and there is a general variation in Fe:Ni ratio in Western Australian komatiite-associated nickel deposits (Marston *et al.* 1981). Recent publications have stressed the importance of the nature and composition of the komatiite host-rocks to the Kambalda nickel deposits (Hupfert *et al.* 1984, Lesher *et al.* 1981, 1984). However, few genetic models have considered the significance of this variation in sulfide composition.

This paper is based on a large and comprehensive data-base of Fe, Ni, S, Cu, Co, Cr, Zn, As, Pb, Bi

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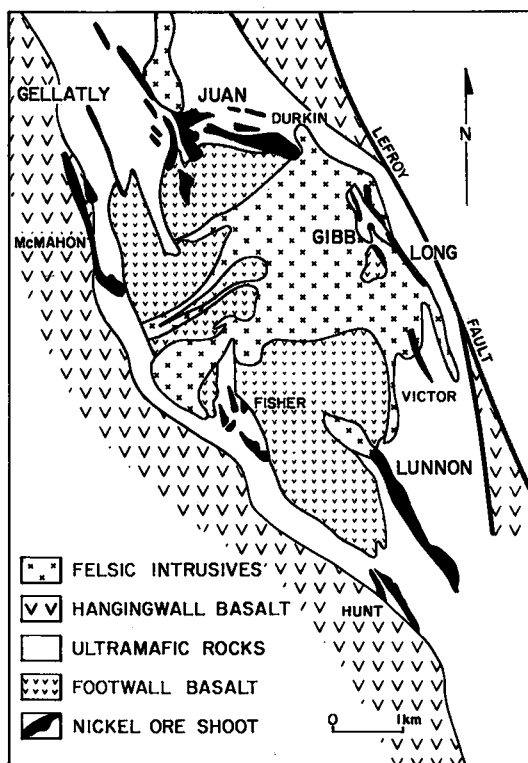


FIG. 1. Simplified geological plan of the Kambalda Dome showing the positions of the major orebodies in plan projection. Orebodies sampled in this study are in bolder type.

and Ag concentrations in Kambalda ores, covering the complete range of compositions observed at Kambalda. The data are interpreted in terms of the model of Woolrich *et al.* (1981), which explains compositional variation in terms of disequilibrium in oxygen fugacity between sulfide and silicate melts prior to eruption and emplacement.

GEOLOGY OF THE KAMBALDA NICKEL FIELD

Kambalda is located within the Norseman-Wiluna greenstone belt in the Archean Yilgarn block of Western Australia. The stratigraphy and general geology of the Kambalda nickel field are reviewed by Gresham & Loftus-Hills (1981) and Marston (1984); only those aspects of the deposits that are of direct relevance to this paper will be outlined here. In the Kambalda area (Fig. 1), the sequence comprises three major conformable formations: footwall basalts, komatiites, and hanging-wall basalts. The Kambalda area has been metamorphosed to the low amphibolite facies, and deformation is heterogeneous and nonpenetrative (Binns *et al.* 1976, Barrett *et al.* 1977).

Ore occurs as thin, tabular concentrations of iron-nickel sulfide and is restricted to the lowermost units in a thick pile of komatiite lava flows (Fig. 2). Ore occurs in 24 discrete complexes or 'shoots' (Fig. 1) composed of one or more 'orebody'. Orebodies are discrete tabular sulfide bodies that occur in three stratigraphic or structural settings: contact ore, hanging-wall ore, and offset ore (Fig. 2). Ores are further classified on the basis of their Ni-tenor

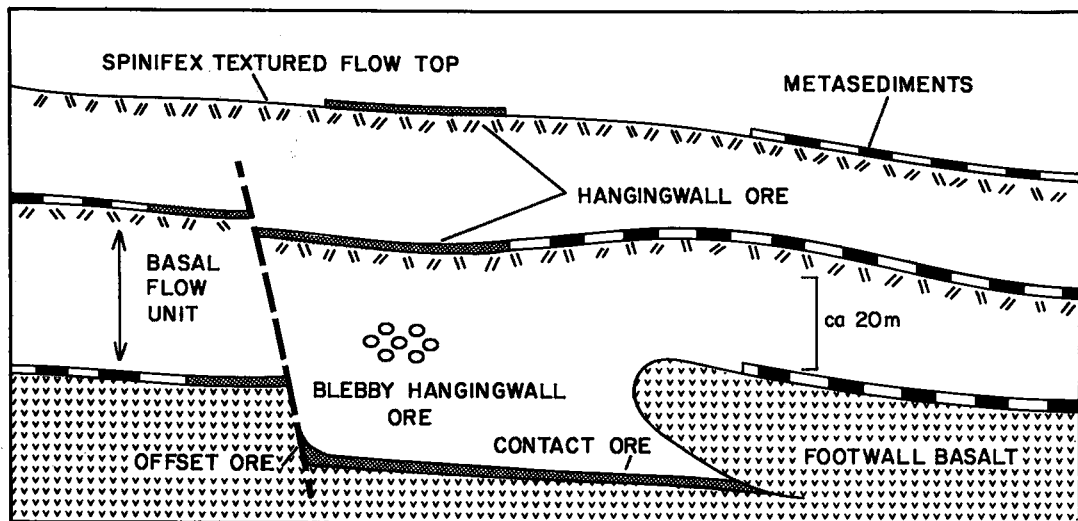


FIG. 2. Schematic cross-section through a typical Kambalda ore position showing the three major settings for nickel ores. The partial confinement of ore to a depression in the footwall basalt - ultramafic rock contact is typical of Kambalda troughs.

(Woolrich & Giorgetta 1978, Woolrich *et al.* 1981), which is defined as the Ni content in 100% sulfides. Three categories are used: low tenor (less than 8% Ni), medium tenor (8 to 14% Ni), and high tenor (greater than 14% Ni).

Contact orebodies occupy a position at the base of the lowermost flow unit overlying the footwall basalt and are typically confined, at least in part, to 'troughs' in the footwall (Fig. 2; see also Gresham & Loftus-Hills 1981). These ores account for the majority of the metal reserves around the Kambalda Dome (Gresham 1986) and occur as large, thick (2–4 m), medium-tenor orebodies such as Lunnon Main Contact (Ross & Hopkins 1975), Juan Main (Marston & Kay 1980) and Long (Gresham & Loftus-Hills 1981).

Hanging-wall ores occur at the base of the second komatiite flow in the sequence or, rarely, at the base of the third or fourth flow (Fig. 2). Most hanging-wall orebodies are spatially related to contact orebodies and typically overlie them (Gresham & Loftus-Hills 1981). The hanging-wall ore zone is generally thinner than that of contact ores (0.5 to 1 m) and is commonly, but not always, higher in nickel tenor

(*e.g.*, the Lunnon hanging-wall surfaces: Ross & Hopkins 1975).

Offset ores have been structurally emplaced either into the footwall or hanging-wall of the main ore horizon (Fig. 2). They comprise a minor, but locally important, component of the reserves of nickel ore.

Ore zones are generally thin (1 to 5 m) and comprise varying proportions of massive sulfides (greater than 80% sulfide), matrix sulfides (40–80% sulfide), heavy disseminated sulfides (10 to 40% sulfide) and light disseminated sulfides (less than 10% sulfides) (Fig. 3). Woodall & Travis (1969) noted the persistent stratification of the ore zone into massive sulfides overlain by matrix sulfides, which in turn may be overlain by disseminated sulfides (Fig. 3). However, these individual types of ore can occur in isolation, especially in areas of extreme structural dislocation.

Massive sulfides are most abundant in contact ores, where they form an irregular and discontinuous layer resting on the footwall basalt. Massive sulfides are heterogeneous, comprising banded pyrrhotite–pentlandite and discrete lenses or bands of pyrite within or at the margins of the layer (Woodall &

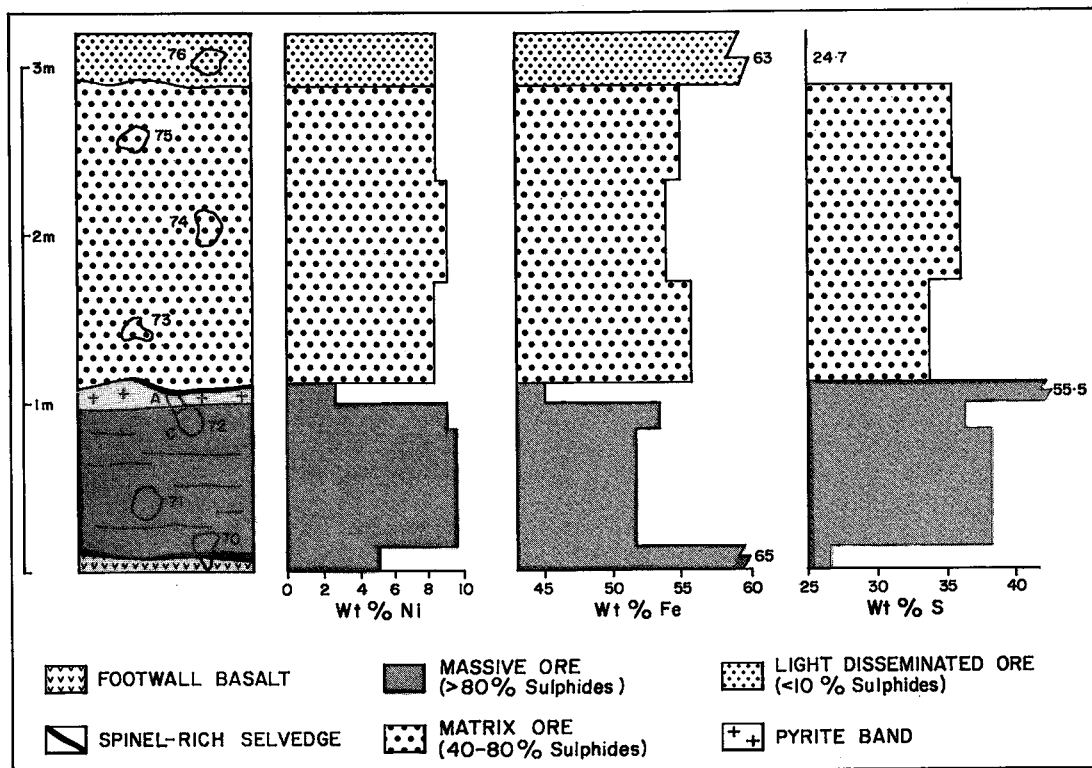


FIG. 3. Sketch of a typical section through the Lunnon Main contact (location: 4-level ore drive, 546507N, 374379E + 202 m R.L.) showing textural variations and location of samples (Numbers refer to A.C. thesis collection; see Cowden 1986). The diagram also shows the variation in Ni, Fe and S, recalculated to 100% sulfides plus oxides, through this ore section.

Travis 1969, Ewers & Hudson 1972, Marston & Kay 1980, Cowden & Archibald 1987; Fig. 2). Discrete magnetite- and chromite-rich zones occur at the top and bottom of most massive-sulfide layers (Groves *et al.* 1977).

Matrix and heavy disseminated sulfides form a more continuous and thicker layer than massive sulfides and are much more homogeneous in texture. Pyrite is less common, and magnetite, more abundant (Ewers & Hudson 1972, Cowden 1986).

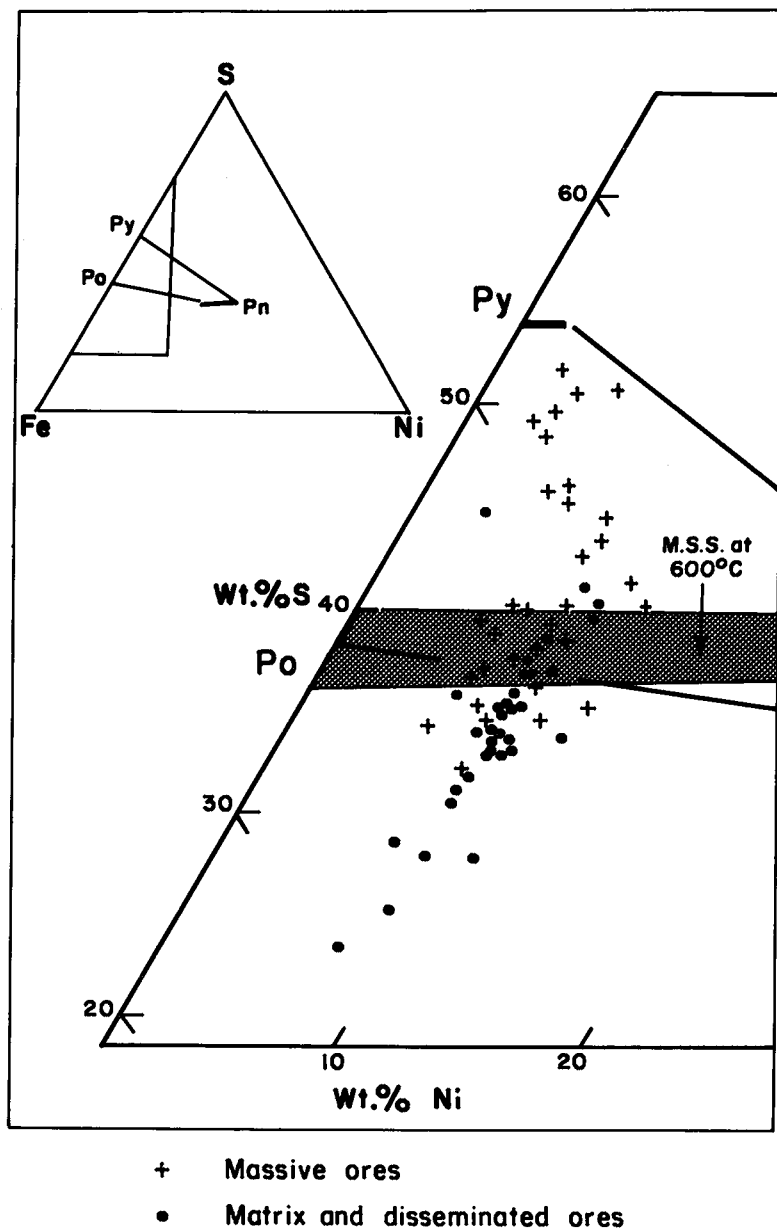


FIG. 4. A plot of the 100% sulfide-oxide composition of all samples from the Lunn contact orebodies on a portion of the Fe-Ni-S triangular diagram. Massive-sulfide samples are shown by crosses, matrix and disseminated sulfide samples are shown by circles. The field of monosulfide solid-solution (*Mss*) at 600°C is shaded.

DATA COLLECTION AND PRESENTATION

Samples were collected from eight orebodies that were selected to cover the range of compositions, styles of mineralization and geological settings of the Kambalda deposits. The orebodies sampled are described in Table 1; their locations are also given in Figure 1 (Gresham & Loftus-Hills 1981). Where underground workings permitted, samples were collected from sections through the ore zone, with one or more samples (1 to 2 kg) being taken from each type of ore. In total, the data base consists of 312 samples from 70 sample sections through the eight orebodies listed in Table 1.

Each sample was crushed to minimize the effects of mineral heterogeneity in these coarse-grained rocks. Splits for chemical analysis were pulverized in a tungsten carbide bowl, and those for X-ray diffraction analysis, in Western Mining Corporation's Fluid Energy Mill (see Hooten & Giorgetta 1977). Fe, Ni, Cu, Co and Zn were determined by atomic-absorption spectrophotometry (A.A.S.) following a mixed-acid leach (HClO_4 , HNO_3 , HF, HCl, H_2SO_4). Arsenic was determined by a colorimetric technique following arsine extraction.

Silver, Bi and Pb were determined by A.A.S. following solvent extraction. Chromium was determined by A.A.S. following fusion with NaOH and subsequent digestion in HCl. Sulfur was determined by the Leco method. Internal standards were used to monitor accuracy, and all samples were analyzed in duplicate. Only those analytical results with a precision better than $\pm 10\%$ were accepted.

All analyses were recalculated to 100% sulfides plus oxides using the method of Cowden (1986). This method recognizes that the abundant magnetite in matrix and disseminated ores is genetically linked to the sulfides and should, therefore, be included in any recalculation procedure. Most investigators agree on the link between sulfides and oxides. However, some propose a metamorphic origin for the bulk of the oxides (e.g., Groves *et al.* 1977), whereas others suggest a magmatic origin (e.g., Ewers & Hudson 1972, Woolrich *et al.* 1981).

The recalculation procedure involves the subtraction of Fe in the gangue phases (*i.e.*, those other than sulfides and oxides) from the initial whole-rock composition and recalculation of the remaining Fe and the chalcophile elements to 100%. A small proportion of the oxide phase is derived from serpentinization of olivine; a correction factor based on the mass-balance equations of Donaldson (1983) is incorporated into the recalculation procedure to account for this. The absolute amount of Fe in the gangue phases is calculated from known compositions of minerals and XRD-determined modal mineralogy. The XRD method is described by Hooten & Giorgetta (1977) and Mitchell (1984). Analytical errors

TABLE 1. GEOLOGICAL SETTING OF ORE BODIES SAMPLED

ORE BODY	TENOR	GEOLOGICAL SETTING
Lunnon Main	low-medium	large, thick contact ore body
Lunnon Top Surface East	medium	structurally dislocated continuation of Main Contact
Lunnon Hangingwalls	high	large hangingwall ore body directly overlying Lunnon contacts at base of second flow unit
Juan West 10C	high	small contact ore body
Juan West 11C	medium	as for 10C, adjacent and parallel plunge
Long Shoot	medium	large thick contact ore body, high proportion massive ore
Gibb Shoot	very high	small, deformed millerite-bearing contact ore body adjacent to Long Shoot
Gellatly Shoot	medium	small relatively undeformed contact ore body

are magnified by this recalculation technique; consequently, only those values with a calculated precision of better than $\pm 20\%$ were accepted.

The variability in the relative proportions of massive, matrix and disseminated sulfides, and the highly heterogeneous nature of massive sulfides (Cowden & Archibald 1987), make it difficult to determine a bulk composition of the ore for any particular point within an ore surface. For this reason, composite samples of mine production were used by Woolrich & Giorgetta (1978), Ross & Keays (1979) and Woolrich *et al.* (1981) to estimate the composition of the Kambalda ores. Such samples, however, are usually a mixture of ores from ore surfaces of different compositions and geological settings within one mine. The approach taken in this study was to calculate the composition of each sample profile using all samples collected from that profile. Each sample was weighted with respect to its influence on the total composition of the sample profile and to its percentage of contained sulfides and oxides. By using this method, samples of pyrite- or spinel-rich bands did not have an undue influence on the bulk composition of the ore profile.

GEOCHEMISTRY

The chemistry of the Kambalda nickel ores is dominated by Fe, Ni and S, which comprise 98% of the ore. There are minor amounts of Cu, Co, Cr, Zn and O, and trace amounts of As, Pb, Bi, Ag and the precious metals (Pt, Pd, Au, Os, Ir, Rh, Ru).

Variation within ore bodies

One of the most important features of the Kambalda ores is the contrast in chemistry and mineralogy between massive and matrix-

disseminated sulfides within any given ore-zone. This contrast is highlighted by the recalculated composition of all samples from the Lunnion Main contact orebody (Table 1) plotted in Figure 4. These data indicate that matrix and disseminated sulfides have a lower S-content than massive sulfides (Fig. 4) and that most samples plot along a line of constant Fe:Ni ratio.

This chemical variation is reflected in the mineralogy of the rocks; matrix and disseminated sulfides consist of pyrrhotite – pentlandite – magnetite, whereas massive sulfides comprise pyrrhotite – pentlandite – pyrite (Cowden 1985). The magnetite-rich nature of matrix and disseminated sulfides has also been reported by other investigators (Ewers & Hudson 1972, Groves *et al.* 1977), and the high content of pyrite in massive sulfides is reflected in reports of thick pyrite bands and lenses (Woodall & Travis 1969, Ewers & Hudson 1972, Marston & Kay 1980, Seccombe *et al.* 1981). Most of the 70 ore sections sampled show a similar contrast between matrix-disseminated and massive sulfides (Cowden 1985, 1986).

The variable S-content within an orebody (Fig. 1)

mainly reflects the contrast in mineralogy and chemistry between pyrite-rich massive sulfides and magnetite-rich matrix-disseminated sulfides. This variation is interpreted by Cowden (1985, 1986) to be the result of metamorphic oxidation of pyrrhotite in matrix and disseminated sulfides, producing magnetite and sulfur-rich fluids. Sulfidation of pyrrhotite to pyrite at the margins of massive sulfides by these S-rich metamorphic fluids produced pyrite-rich layers (Seccombe *et al.* 1981, Cowden & Archibald 1987). However, Ewers & Hudson (1972) suggested that the high content of magnetite in the matrix and disseminated sulfides is a magmatic effect due to *in situ* fractionation and re-equilibration during cooling. Woolrich *et al.* (1981) also suggested that magnetite is magmatic in origin, resulting from variations in $f(\text{O}_2)$ and $f(\text{S}_2)$ during cooling. Although this variation in sulfur content between massive and matrix-disseminated sulfides is an intriguing problem, it is nevertheless a local variation. Its relevance to this study is the large-scale variation in Fe:Ni ratio between orebodies. The variable content of sulfur is dealt with by Cowden (1985, 1986) and Cowden & Archibald (1987). It is important to recog-

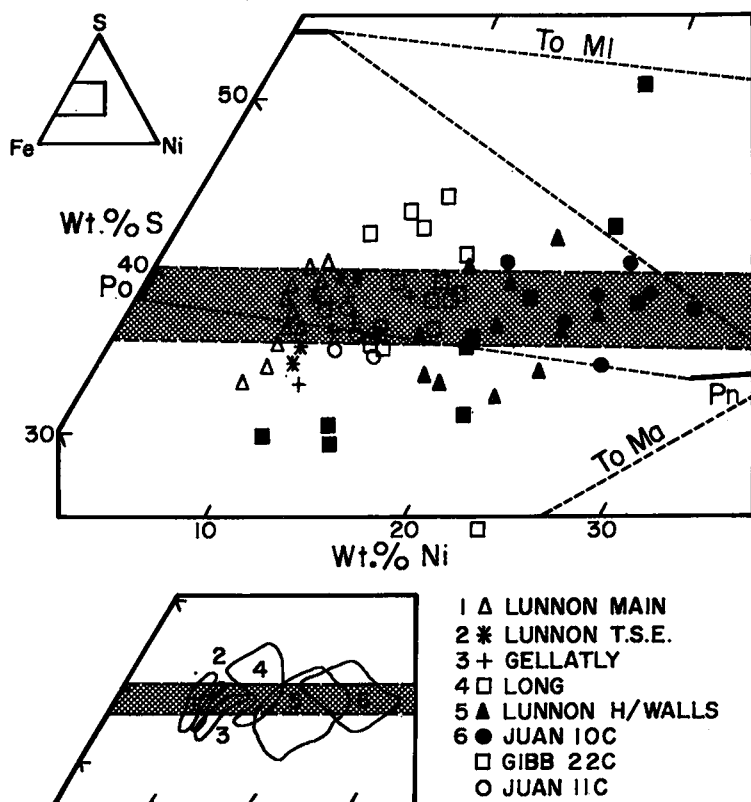


FIG. 5. Plot of average 100% sulfide-oxide compositions of all ore sections sampled on a portion of the Fe-Ni-S triangular diagram and a summary of all ore-surface compositions. The field of *Mss* at 600°C is shaded.

TABLE 2. AVERAGES OF THE WEIGHTED MEAN COMPOSITIONS OF ORE PROFILES FROM KAMBALDA ORE BODIES

	Fe	Ni	S	Cu	Co	Cr	Zn	S/Ni	Fe/Ni	Ni/Cu	Ni/Co	Met/S
LUNNON MAIN CONTACT	53.9 (2.2)	8.3 (0.6)	36.5 (2.3)	0.81 (.06)	0.20 (.03)	0.27 (.21)	.044 (.023)	4.20 (.99)	6.57 (.61)	10.2	41.5	1.74 (.17)
LUNNON TOP SURFACE EAST	52.0 (2.1)	9.8 (.04)	37.1 (2.2)	0.64 (.39)	0.21 (.02)	0.22 (.19)	.040 (.010)	3.78 (.27)	5.2 (.36)	45.3	46.7	1.70 (.16)
GELLATLY	50.8 (2.5)	11.3 (1.09)	36.2 (1.7)	1.26 (.70)	0.26 (.03)	0.31 (.07)	.027 (.019)	3.24 (.30)	4.57 (.56)	9.0	49.14	1.78 (.16)
JUAN WEST 11C	50.5 (1.35)	11.1 (1.9)	36.6 (2.1)	1.06 (1.2)	0.23 (.10)	0.46 (.16)	.043 (.022)	3.15 (.45)	4.37 (.51)	10.5	48.3	1.73 (.15)
LONG	46.0 (2.4)	13.6 (1.8)	38.8 (2.7)	1.14 (.55)	0.28 (.06)	0.18 (.10)	.034 (.028)	2.94 (.61)	3.46 (.56)	11.9	48.6	1.58 (.18)
GIBB	44.7 (9.3)	18.3 (5.4)	34.1 (6.3)	1.30 (.79)	0.29 (.09)	0.69 (.34)	.037 (.017)	1.94 (.55)	2.70 (1.34)	14.1	63.1	2.50 (.52)
LUNNON HANGING WALLS	43.3 (3.8)	18.7 (2.5)	35.4 (3.1)	1.10 (.49)	0.31 (.11)	1.45 (1.29)	.101 (.067)	1.96 (.40)	2.37 (.48)	17.0	60.3	1.81 (.22)
JUAN WEST 10C	38.4 (3.2)	22.6 (5.2)	37.4 (2.0)	0.96 (.60)	0.26 (.06)	0.43 (.25)	.041 (.022)	1.70 (.32)	1.76 (.40)	23.5	86.9	1.67 (.14)

Standard deviations in brackets

All values recalculated to 100% sulfides plus oxides.

nize that for the purpose of this paper, Ni-tenor does not vary markedly within an orebody.

Variation between Kambalda orebodies

Having established the nature of the geochemical variation within an orebody, it is possible to examine the compositional variation between orebodies by using the weighted average compositions for each ore section calculated by the method outlined above. The calculated compositions for each section are plotted on a portion of the Fe-Ni-S triangular diagram in Figure 5. Most compositions plot within, or close to, the field of monosulfide solid-solution (*Mss*) at 550°C (Naldrett *et al.* 1967). Figure 5 indicates that Ni-tenor does not vary greatly between ore sections from one orebody, especially low-tenor orebodies, but that the Ni-tenor and Fe:Ni ratio do vary significantly between orebodies. Compositions of individual sections from any one orebody also vary in S content. This variation is probably a reflection of the variable proportion of massive and matrix-disseminated sulfides within the section (Cowden 1985, 1986). This variation may also be related to the variable development of spinel- or pyrite-rich horizons. The two contrasting geochemical variations are highlighted in Table 3, which indicates that there is a strong negative correlation between Fe and Ni and an independent negative correlation of S and Fe.

The composition of each orebody sampled is listed in Table 2. These compositions are simple arithmetic averages of the weighted average composition of each ore profile from a particular ore surface. These data indicate that for most orebodies, except Gibb, the ratio of total metals to sulfur is remarkably constant, and that all orebodies show systematic increases

in Cu, Co, Ni/Cu and corresponding decreases in Fe, S/Ni and Fe/Ni as Ni tenor increases.

The data presented in Tables 2 and 3, and in Figure 5 indicate that there are two independent variations in geochemistry. There is a strong negative correlation between Fe and S, which reflects the variation in S content within individual orebodies, and also

TABLE 3. CORRELATION COEFFICIENTS FOR ORE-SECTION COMPOSITIONS

	Fe	Ni	S	Cu	Co	Cr	Zn	Cu/Ni	Co/Ni	Met/S
Fe	1.00	-.70	-.72	-.28	-.34	-.17	-.12	-.14	-.27	.63
Ni		1.00	.02	.10	.28	.38	.29	.32	.32	.03
S			1.00	.19	-.18	-.22	-.18	-.04	-.8	-.93
Cu				1.00	.16	-.07	.05	-.56	.26	-.14
Co					1.00	.30	.31	.01	-.44	-.10
Cr						1.00	.61	.15	-.01	-.19
Zn							1.00	-.05	.01	.20
Cu/Ni								1.00	.01	.02
Co/Ni									1.00	-.06
Met/S										1.00
MEANS	48.5	14.0	35.8	1.05	.25	.44	.05	19.2	64	1.85

TABLE 4. SUMMARY OF THE COMPOSITIONAL VARIATION WITHIN THE KAMBALDA NICKEL DEPOSITS

Element	Range	Element Ratio	Range
Fe	54 to 38%	Ni/Fe	0.15 to 0.57
Ni	8 to 22%	Ni/S	0.24 to 0.59
S	39 to 35%	Ni/Cu	9 to 24
Cu	0.6 to 1.3%	Ni/Co	41 to 87
Co	0.2 to 0.3%	Cu/Co	3.6 to 4.5
Cr	0.18 to 0.4%	Metals/S	1.58 to 2.0
Zn	0.02 to 0.04%	Cr/Zn	9 to 10
As	5 to 20 ppm		
Pb	15 to 25 ppm		
Bi	5 to 10 ppm		
Ag	2 to 4 ppm		

between Fe and Ni, which reflects the gross Fe/Ni variation between orebodies. These correlations might be attributed to autocorrelation of Fe, Ni and S, which are the major components of the ores. However, there is no correlation of Ni with S, so that these two variations are probably independent and probably reflect two distinct geological processes. Woolrich & Giorgetta (1978), Ross & Keays (1979) and Woolrich *et al.* (1981) described gross variations in the Kambalda ore chemistry and showed positive correlations of Cu, Co, Pt and Pd with Ni tenor. This study allows a broader view; the inclusion of Fe shows its negative correlations with all elements (Table 3). Cowden *et al.* (1986) show a similar negative correlation between Fe and the platinum-group elements (Pt, Pd, Os, Ir, Rh and Ru).

Fe is therefore the controlling variable of the sulfide-oxide compositions at Kambalda. The ratio of total metals to sulfur is approximately constant among orebodies, but chalcophile elements in 100% sulfide-oxides increase as the Fe content decreases. The compositional variability among the Kambalda deposits is summarized in Table 4.

The average bulk-compositions of Western Australian dunite-associated deposits and other komatiite-associated nickel deposits (Groves & Hudson 1981) are coincident with the field enclosing all ore-section compositions at Kambalda (Fig. 6). Variable geochemistry, particularly the Fe/Ni ratio, is therefore a feature common to all komatiite-associated nickel deposits.

INTERPRETATION OF THE GEOCHEMISTRY OF THE KAMBALDA ORES

Barrett *et al.* (1977) suggested that metamorphic processes may modify the Fe:Ni ratio of nickel sulfide ores. Metamorphic models to account for the variation in the Fe:Ni between orebodies are rejected because orebodies of contrasting tenor can occur in identical tectonic and metamorphic settings. For example, Marston & Kay (1980) and Woolrich *et al.* (1981) described how Kambalda orebodies can be reconstructed into two parallel belts of orebodies of contrasting tenor. These belts are deformed by all recognized deformational events (N.J. Archibald, pers. comm., 1985) and do not coincide with separate areas of serpentinite or carbonate-altered ultramafic rocks.

Composition of the silicate liquid

Rajamani & Naldrett (1978) demonstrated that sulfide composition is controlled by the composition of the silicate liquid. Their experiments outlined the broad chemical controls on metal distribution between sulfides and silicates. Their results are plotted in Figure 7. Duke & Naldrett (1978) and Duke (1979) produced computer models of the variation in chemistry of sulfide liquids separating from a fractionating silicate magma. The range of these sulfide compositions that most closely models the actual variation at Kambalda is produced from a melt frac-

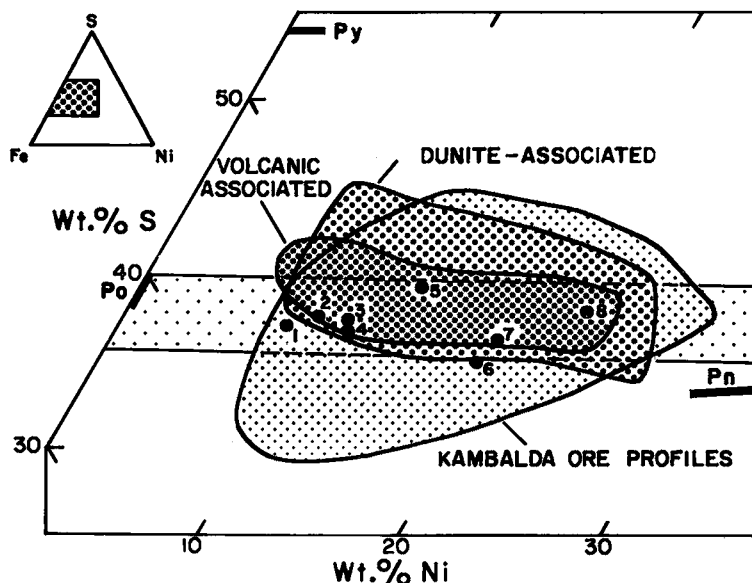


FIG. 6. A comparison of the field enclosing Kambalda ore-surface and ore-section compositions with those enclosing the compositions of other Western Australian volcanic-rock-associated deposits and dunite-associated deposits (from Marston *et al.* 1981). The lightest stipple is the field of Mss at 600°C.

tionating olivine and sulfide in the ratio 100:1 (Fig. 7). Also plotted in Figure 7 is the range of Kambalda sulfide compositions defined in this study and the range of initial compositions of komatiite liquid (28 to 32% MgO) calculated by Lesher (1983). These data show that both models, especially that of Rajamani & Naldrett (1978), require extreme amounts of fractionation in order to account for the range of compositions of Kambalda ore. The Duke & Naldrett (1978) model gives the better fit, but requires 50% fractionation to 22% MgO to account for the observed variation in Ni content. There is no evidence for extensive fractionation of the liquids from which the hosts to the nickel sulfide mineralization were derived (Lesher 1983). Therefore, variability in host-rock composition cannot explain the compositional diversity of the sulfides.

Mass-balance effects

Mass-balance effects have also been invoked to account for deviations in sulfide composition from those predicted by published partition-relationships, e.g., in the Pipe deposit (Campbell & Naldrett 1979), Moxie Pluton (Thompson & Naldrett 1984), and the Stillwater and Bushveld complexes (Campbell *et al.* 1980).

The partitioning of elements between sulfide and silicate liquids is described by the Nernst equation:

$$Y_i = X_i \cdot D_i \quad (1)$$

where Y_i is the abundance of element i in the sulfides, X_i the abundance of i in the silicate and D_i the Nernst distribution coefficient. Where the mass ratio of sulfide to silicate is high, normal partition relationships do not hold, and the following modified equation must be used (Campbell & Naldrett 1979):

$$Y_i = X_i \cdot D_i (R+1)/(R+D_i) \quad (2)$$

where R is the mass ratio of silicate magma to sulfide melt. The effect of variable R on the composition of equilibrium sulfide melts has been modeled by Campbell & Naldrett (1979), who found that the concentration of any chalcophile element decreases rapidly with decreasing R .

Naldrett (1981) modeled the composition of Lunnon shoot ores reported by Ross & Keays (1979) and calculated a relatively low R value of 316. Using Naldrett's parameters, the effect of variable R on sulfide compositions has been calculated and plotted in Figure 8, together with all published orebody com-

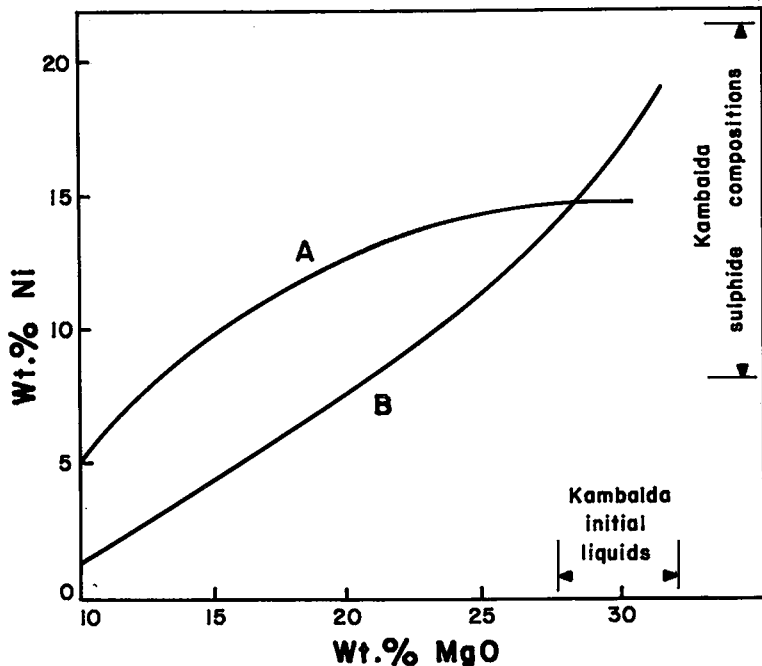


FIG. 7. A plot of wt. % nickel in sulfide liquid versus the wt. % MgO in silicate liquid at equilibrium. A. Equilibrium crystallization as modeled by Rajamani & Naldrett (1978). B. Fractionation of olivine and sulfide in the ratio 100:1 as modeled by Duke & Naldrett (1978) and Duke (1979).

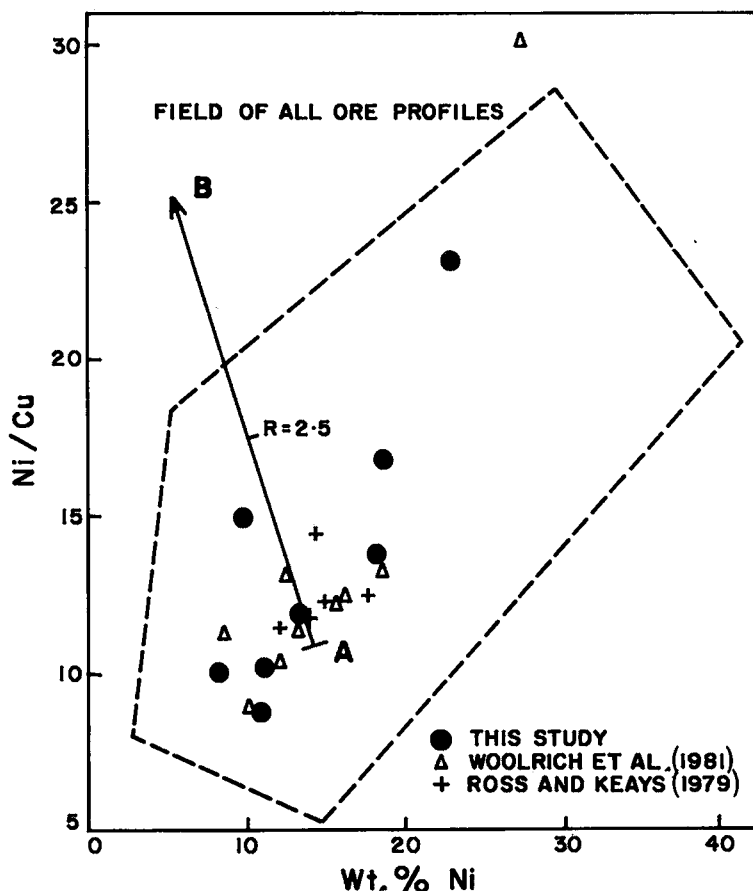


FIG. 8. A plot of Ni versus Ni/Cu ratio for all 100% sulfide-oxide compositions determined for Kambalda ore surfaces. The field of Kambalda ore profiles is also marked to further define the trend of increasing Ni/Cu with increasing Ni tenor. The line A-B is the line of compositions predicted by the R model of Naldrett (1981).

positions and the results of this study. It is clear from Figure 8 that this model cannot account for the variation in sulfide compositions at Kambalda.

Given that the values of D used by Naldrett (1981) are poorly constrained (see discussion in Campbell *et al.* 1983 and Campbell & Barnes 1984) and that the values of R are unknown, equation 2 above has no unique solution. In order to further evaluate this model, the variation in Ni, Cu, Co and Pt contents of sulfide liquids with varying R has been calculated using Lesher's (1983) composition of the initial liquid to estimate X_{Ni} , X_{Cu} and X_{Co} . X_{Pt} was estimated from the data of Campbell & Barnes (1984). Curves that model the full range of Kambalda sulfide compositions with D varying from the minimum value to infinity are plotted in Figure 9. These data indicate that using best estimates of X_i and no matter what combination of D and R used, variable R can-

not model the variation in sulfide compositions observed at Kambalda.

The role of oxygen fugacity

Woolrich & Giorgetta (1978) first suggested that variable $f(O_2)$ in a sulfide-silicate system could produce the diversity in nickel tenors observed at Kambalda. Woolrich *et al.* (1981) presented an analogy with Cu smelting slags and postulated that small variations in $f(O_2)$ would change thermodynamic parameters and affect the partitioning behavior of Fe. Oxidation is interpreted to upgrade nickel sulfides by the preferential partitioning of Fe to the silicate liquid. Campbell *et al.* (1980) also found, in a series of experiments on komatiite liquids, that the partitioning of metals in such systems is controlled by the ratio of $f(O_2)/f(S_2)$.

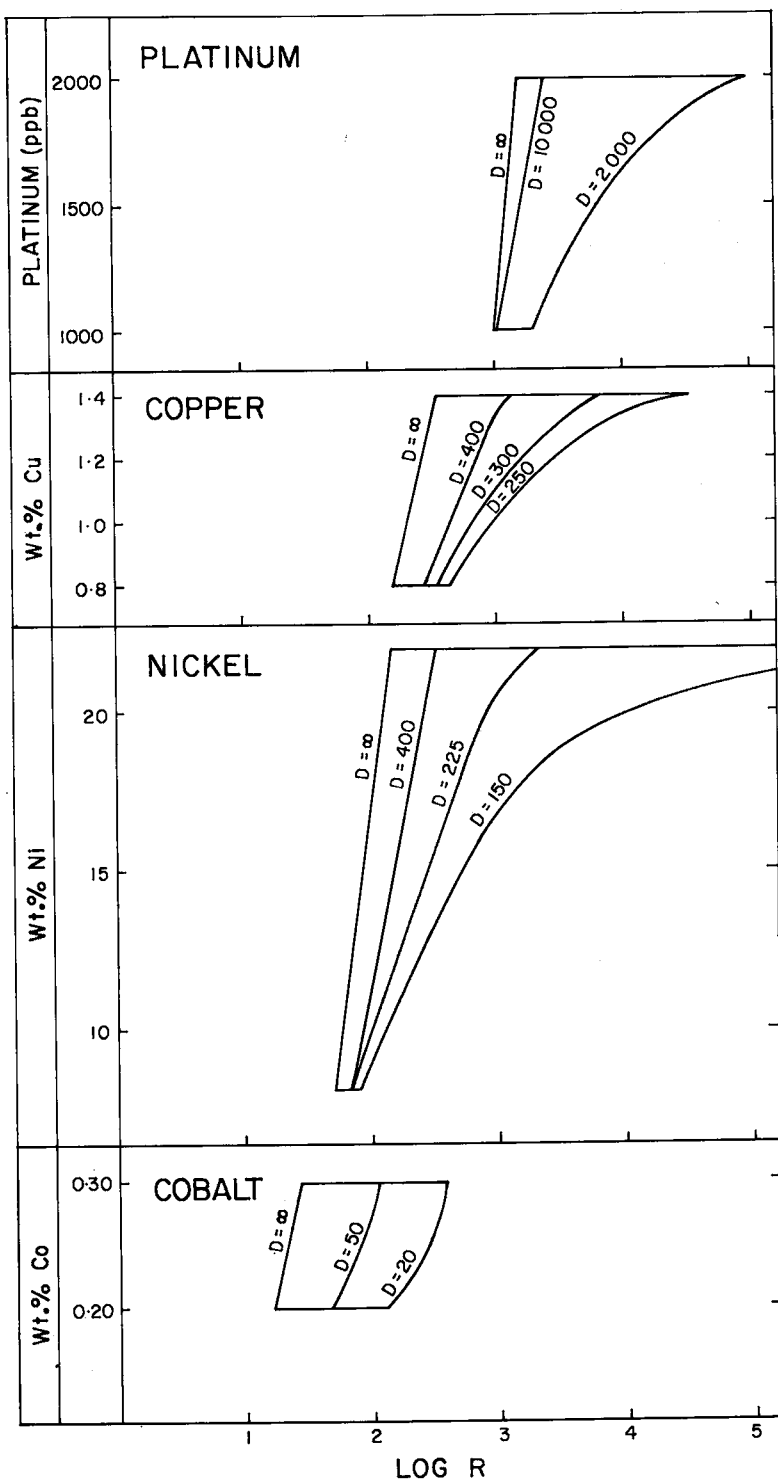


FIG. 9. Portions of the curves that describe the variation in Ni, Pt, Cu and Co content of equilibrium sulfide liquids as a function of R (see text for explanation of R). Curves are presented for the range of metal contents in Kambalda ores defined in this study (see Table 4) and for the minimum value of D to the maximum. Values of X_{Ni} (1600 ppm), X_{Cu} (50 ppm) and X_{Co} (114 ppm) are from Leshner *et al.* (1981); the value of X_{Pt} (10 ppb) is from Campbell *et al.* (1983).

Partitioning relations between sulfides and silicates have been explained in terms of crystal- and ligand-field theories by Burns (1970), MacLean & Shimazaki (1976) and Rajamani & Naldrett (1978). Can these theoretical models also explain the role of oxidation, if any, in modifying partition relationships? Chalcophile transition elements such as Ni, Cu, Co and the PGE are most stable in octahedrally co-ordinated sites and have high octahedral site-preference energies (O.S.P.E.) (Burns 1970). Metals in a sulfide liquid are interpreted to be in octahedral co-ordination (Naldrett 1969). The number of octahedral sites available to elements such as Ni in a silicate liquid is dependent upon the structure and bulk composition of that liquid.

Limited oxidation at low partial pressures of oxygen will not greatly alter the structure of a sulfide melt (Ubbelohde 1965, Rajamani & Naldrett 1978) owing to the very limited solubility of oxygen in sulfide liquids (Naldrett 1969). However, increased $f(\text{O}_2)$ may markedly alter the structure of silicate melts. Hess (1980) suggested that Fe^{3+} is restricted to tetrahedral sites, whereas Fe^{2+} occurs in both tetrahedral and octahedral sites, and concluded that $\text{Fe}^{2+}/\text{Fe}^{3+}$ is proportional to $\log f(\text{O}_2)$. Oxidized, silica-rich melts are dominated by tetrahedral sites, whereas basic, relatively unoxidized liquids are characterized by more octahedral sites (Whittaker 1967, Burns & Fyfe 1964, Rajamani & Naldrett 1978, Hess 1980). It is therefore reasonable to conclude that oxidation will reduce the number of octahedral sites in a komatiite liquid.

How does this reduction in number of octahedral sites affect partitioning relationships? Ni^{2+} has a O.S.P.E. of 20.4 compared to 4 for Fe^{2+} (Dunitz & Orgel 1957). If the number of six-fold co-ordinated sites in the silicate liquid is reduced (e.g., upon oxidation), Ni^{2+} will have a stronger tendency than Fe^{2+} to leave the silicate liquid for the abundant octahedral sites in the sulfide liquid and thereby will increase the Ni content of the sulfide liquid. Oxidation will also change the valency of some Fe^{2+} ions to Fe^{3+} ; consequently, the number of Fe ions available for partitioning to sulfide is reduced, as Fe^{3+} does not partition to sulfides. The multiplying effect of the partition coefficient will enhance this reduction in Fe^{2+} . These complementary processes combine to increase the Ni content and decrease the Fe content of the sulfide liquid upon oxidation.

Throughout this discussion it has been tacitly assumed that the sulfur content of the sulfide liquid remains constant with varying $f(\text{O}_2)$. This is supported by Naldrett (1969), who demonstrated that silicate liquids buffer the composition of sulfide liquids and that at low $f(\text{O}_2)$ in realistic geological systems, small variations in $f(\text{O}_2)$ will not change the metal-sulfur ratio.

Quantitative modeling of the variation in sulfide

composition caused by oxidation is difficult owing to limited thermodynamic data for komatiites. To highlight the potential significance of $f(\text{O}_2)$ in controlling sulfide compositions, a model is briefly outlined below.

Two sulfide-silicate systems, A and B, which have identical host-silicate liquid compositions, but contrasting equilibrium values of $f(\text{O}_2)$, are equated to model the change in the equilibrium sulfide composition. The exchange reaction



describes the partitioning of the major elements in such systems, and the equilibrium constant K for this reaction is

$$K = a_{\text{NiS}} \cdot a_{\text{FeO}} / a_{\text{NiO}} \cdot a_{\text{FeS}} \quad (4)$$

The equilibrium constants for (3) will be equivalent in the two systems and, therefore, the expressions can be equated. If we assume that FeS/NiS is constant with varying sulfide composition (e.g., Toulmin & Barton 1964, Rajamani & Naldrett 1978), then we can write

$$\frac{X_{\text{NiS}}}{X_{\text{FeS}}} \cdot A \cdot \frac{X_{\text{NiS}}}{X_{\text{FeS}}} \cdot B = \frac{a_{\text{NiO}}}{a_{\text{FeO}}} \cdot A \cdot \frac{a_{\text{FeO}}}{a_{\text{NiO}}} \cdot B \quad (5)$$

Equation 5 relates the equilibrium sulfide compositions to thermodynamic parameters. The relationship of a_{NiO} to $f(\text{O}_2)$ can be estimated using the data of Campbell *et al.* (1979), and the relationship of $f(\text{O}_2)$ to a_{FeO} can be extrapolated from work on basaltic compositions (Fudali 1965). Sulfide composition can therefore be related to $f(\text{O}_2)$. If we assume the Lunnion shoot composition for system A and choose values of $f(\text{O}_2)$ in systems A and B, the composition of sulfide in system B can be calculated. Values of $f(\text{O}_2)$ of 10^{-6} and 10^{-7} atm. were chosen based on estimated values in natural systems (Eugster & Wones 1962).

The change in sulfide composition resulting from increasing $f(\text{O}_2)$ by one log unit from -6 to -7 is represented in Figure 10. These data indicate that the entire range of Kambalda ore compositions may be explained by relatively minor variation in $f(\text{O}_2)$.

A MODEL FOR THE GENERATION OF VARIATIONS IN Ni-TENOR

The data and discussion presented above suggest that the Ni/Fe variation between the ore surfaces at Kambalda may be attributed to variable $f(\text{O}_2)$ at the magmatic stage. Woolrich *et al.* (1981) placed oxidation and, consequently, sulfide saturation, prior to eruption (*cf.* Ross & Keays 1979, Bavinton 1979, Groves & Hudson 1981, Leshner *et al.* 1981, Keays *et al.* 1981). Recently, Huppert *et al.* (1984) suggested

that komatiite flows may melt and assimilate sulfur-rich sediments beneath flows, resulting in *in situ* sulfide saturation. Leshner *et al.* (1984) developed this model further and suggested that Ni-tenor variations may be due to variable R within such systems. The R factor has been rejected above as a plausible model to account for the geochemical variation within the Kambalda deposits; however, it could be argued that different equilibrium conditions [$f(\text{O}_2)/f(\text{S}_2)$] in different flow units may result in the variations in Ni-tenor.

Claoue-Long & Nesbitt (1984) and Gresham (1986) presented strong arguments based on field relationships against the ground melting and assimilation hypothesis; Groves *et al.* (1986) argued that only limited thermal erosion is possible. Groves *et al.* (1979) listed evidence for sulfide saturation at depth; all available geochemical data (Woolrich & Giorgetta 1978, Leshner *et al.* 1981) suggest that the whole of the ultramafic sequence at Kambalda is derived from liquids that equilibrated with sulfides. These data are not consistent with the model of Huppert *et al.* (1984). Saturation and separation of sulfide liquids prior to eruption and emplacement are features of our preferred hypothesis.

Komatiites were erupted rapidly (estimated ascent velocity 4.8 m s^{-1} ; Huppert *et al.* 1984). Rapid rates of eruption may have helped to transport droplets of immiscible sulfide from the site of separation and equilibration to the surface. Helz (1977), Huang & Williams (1980) and Wendlandt (1982) have shown that the solubility of sulfur in basaltic magmas increases with decreasing pressure, indicating that exsolution and saturation during ascent would seem unlikely. Sulfide saturation and equilibration may have taken place in the mantle at the site of partial melting; the vigor and speed of eruption were perhaps sufficient to carry entrained sulfide droplets from depth without significant dissolution (settling velocity of a 1-cm droplet is approximately 1 m s^{-1}). Increasing solubility of sulfur and equilibrium values of $f(\text{O}_2)$ upon ascent raises the possibility that sulfides and their silicate-host liquids are in disequilibrium. This disequilibrium between sulfides and silicates may explain the occurrence of ores of contrasting Ni-tenor in host rocks of identical composition.

Wendlandt (1982) suggested that the oxygen content of a sulfide liquid may reflect its depth of equilibration. His experiments demonstrate that oxygen solubility in sulfide liquids decreases as pressure increases, as do the equilibrium values for $f(\text{O}_2)$ and $f(\text{S}_2)$. Therefore, the large volume, medium-tenor ore surfaces such as Juan Main, Long and Lunnon Contact may represent the products of the earliest, most vigorous eruptions, which carried large volumes of sulfides from the greatest depths. These sulfides would have equilibrated at low values of $f(\text{O}_2)$ and

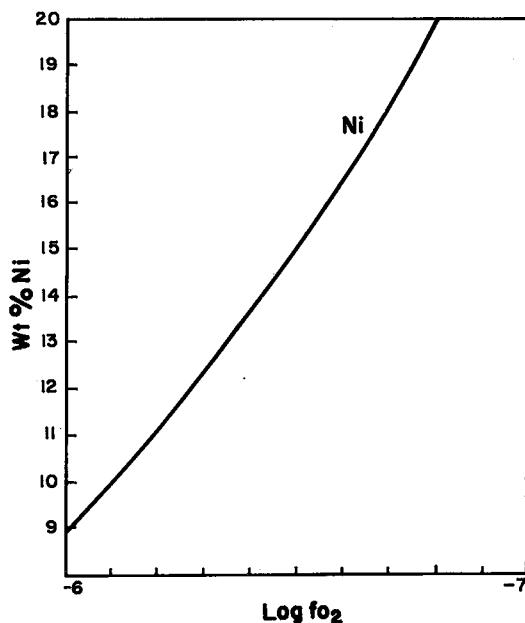


Fig. 10. Model of the variation in Ni in equilibrium sulfide liquid as a function of $f(\text{O}_2)$ (see text for full details).

did not have sufficient time to equilibrate at higher $f(\text{O}_2)$ values upon eruption, and are consequently lowest in Ni. High-tenor ores are typically associated with later flows (*i.e.*, Lunnon and Fisher hanging-wall ores) and are generally much smaller in volume (see Gresham 1986 for a classification of Kambalda ore surfaces). High-tenor ores may therefore represent equilibrium at lower-pressure conditions and may have attained equilibrium with the host rocks. The lower volumes of high-tenor ore surfaces, together with the suggestion of increased solubility of sulfur with time, suggests that these sulfides have undergone some dissolution. Disequilibrium may be enhanced by surface-area effects (*cf.* Woolrich *et al.* 1981); sulfides with a high ratio of volume to surface-area are essentially self-buffering (Naldrett 1969), whereas these with a low ratio will equilibrate quickly with the host liquid. It is interesting to note that relict sulfide blebs within the central portion of flow units are always associated with high-tenor ore surfaces and are always composed of very high Ni-tenor sulfides. These blebs are the most likely compositions to represent equilibrium at near-surface conditions.

The implication of the preceding discussion of the Kambalda geochemical data is that accepted models of sulfide-silicate partitioning cannot adequately explain the diversity of sulfide compositions observed at Kambalda without consideration of the role of $f(\text{O}_2)$. Values of partition coefficients in komatiite-sulfide systems are meaningless unless the

TABLE 5. APPARENT VALUES FOR PARTITION COEFFICIENTS IN KOMATIITE-SULFIDE SYSTEMS CALCULATED FROM KAMBALDA GEOCHEMICAL DATA

Element Partition co-efficient	Range	Published values
D Fe	7 to 5	-
D Ni	50 to 140	100
D Cu	120 to 260	250
D Co	18 to 27	40
D Cr	0.61 to 1.36	-

Model komatiite composition of Lesher (1983) and sulfide compositions from this study used to calculate D from the equation $D = X_i/Y_i$. Published values from Naldrett (1981) and Shimazaki and MacLean (1976).

conditions of the system are defined [i.e., $f(\text{O}_2)$, $f(\text{S}_2)$, P , T , bulk composition and R]. Published values of partition coefficients for high-Mg systems are not incorrect, but rather poorly constrained. Apparent values and the range of values for D at Kambalda can be calculated from the sulfide compositions defined in this study and the model komatiite composition of Lesher (1983) (Table 5). However, care must be taken when constructing models of sulfide-silicate equilibria where published partition-coefficient data are used.

Well-controlled experimental data for a range of compositions at varying conditions of equilibrium are required to construct a model to explain how varying $f(\text{O}_2)$ will affect the partition of metals in komatiitic and less magnesian systems.

SUMMARY AND CONCLUSIONS

Metamorphic alteration of pyrrhotite to magnetite in matrix and disseminated sulfides and of pyrrhotite to pyrite in massive sulfides resulted in contrasting sulfur contents of these ore types. This mineralogical and chemical alteration is reflected in a strong negative correlation of Fe and S.

Within any given orebody, there may be marked variation in S content, but generally, there is only limited variation in Ni-tenor. On the other hand, the average Ni-tenor for Kambalda ore surfaces may range from 8 to 22% Ni. This large-scale compositional diversity is reflected by positive correlations of Ni with Cu and Co, and negative correlations of Fe with Ni, Cu and Co. The overall content of sulfur in the ores remains nearly constant as Ni tenor increases.

The gross compositional variation cannot be explained entirely by metamorphic alteration, nor by magmatic fractionation, nor mass-balance models. The preferred model outlined in this paper is that high Ni-tenor ores are considered to reflect systems in which sulfide and silicate are close to equilibrium in terms of $f(\text{O}_2)$, whereas low- and medium-tenor

ores are interpreted to be in disequilibrium with their host rocks. Oxygen fugacity potentially exerts a critical control on the composition of sulfide liquids; oxidation may enhance the partition of Fe to silicate melts by polymerizing this melt and oxidizing Fe^{2+} to Fe^{3+} . Equilibrium $f(\text{O}_2)$ values are interpreted to decrease with depth. Large-volume, medium- and low-tenor sulfides may represent equilibrium compositions at depth. Disequilibrium was enhanced by rapid eruption, emplacement and separation of sulfide and its concentration prior to eruption.

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