MOBILIZATION OF ORE-FORMING ELEMENTS DURING ALTERATION OF DUNITES, MT. KEITH-BETHENO, WESTERN AUSTRALIA

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ABSTRACT

Centrally disposed disseminated Fe–Ni–Cu mineralization occurs in altered dunites from low- to medium-grade metamorphic environments in the Yilgarn Block, Western Australia. In several cases, aqueous, carbonate-bearing fluids have produced broadly zoned alteration with marginal talc-carbonate rocks normally grading inwards into serpentinites with a core of relict, recrystallized dunite in some cases. The mineralogy of sulfides varies sympathetically with alteration type and is controlled by bulk sulfide composition and by Fe-related redox mechanisms; $f(O_2)$ and $f(S_2)$ normally decrease inwards. In the Mt. Keith–Betheno area, relict dunite contains up to 6 wt. % disseminated pentlandite, which provides a basis for comparison which reacted with added external S to precipitate During initial serpentinization there was near-isochemical internal redistribution of ore-forming elements; progressive serpentinization released Fe which reacted with added external S to precipitate additional Fe–rich sulfides with progressively higher S/Se and S/Pd ratios around pre-existing sulfide nuclei. Similar processes operated at Black Swan and probably elsewhere in the Yilgarn Block. Recrystallization to more S-rich sulfide assemblages during progressive carbonation involved the addition of minor As and erratic loss of Ni and some S. Redistribution of Au was also erratic at Mt. Keith–Betheno in contrast to Black Swan where Au appears to have been liberated during replacement of sulfides by carbonate in highly oxidizing acidic, CO_2-rich solutions. The latter potentially represent the source of epigenetic Au lodes higher in the greenstone sequences. Although alteration reactions do not increase, but may depress the Ni tenor of mineralization, the increase in volume of sulfides possibly represents the initial stage in the formation of Fe-rich, massive metamorphic ores in higher grade metamorphic environments of higher strain.

SOMMAIRE

On trouve une minéralisation disséminée Fe–Ni–

Cu au centre d'une massif de dunite altérée dans une partie faiblement à moyennement métamorphisée du bloc Yilgarn, en Australie occidentale. Dans plusieurs cas, un fluide aqueux carbonaté a produit une altération de la dunite en zones larges; les roches périphériques à talc et carbonates passent à des serpentinites vers le centre, où se trouve un noyau de dunite résiduelle, recristallisée par endroits. La minéralogie des sulfures varie avec cette zonation et dépend de la composition globale des sulfures soumis à des processus réduction-oxydation, que caractérise la décroissance de $f(O_2)$ et $f(S_2)$ de la bordure vers le centre. Dans la région du mont Keith–Betheno, la dunite résiduelle contient jusqu'à 6% (poids) de pentlandite disséminée, ce qui permet de la comparer aux agrégats de sulfures et oxides de la dunite altérée. Au début, la serpentinisation a provoqué une redistribution interne quasi-isochimique des sulfures, tandis qu'aux stades plus avancés le soufre d'apport extérieur, réagissant avec le fer libéré par la serpentinisation, forme des sulfures de fer pour lesquels les rapports S/Se et S/Pd sont de plus en plus élevés à proximité des cristaux de sulfures originels. On conclut à l'existence probable de processus analogues en d'autres points de bloc Yilgarn, particulièrement à Black Swan. Une recristallisation en assemblages enrichis en S au cours d'une carbonation progressive implique une légère addition de As et une perte aléatoire de Ni et d'un peu de S. La redistribution de l'or est, elle aussi, aléatoire au mont Keith-Betheno. A Black Swan, par contre, l'or aurait été libéré durant le remplacement des sulfures par des carbonates, sous l'action de solutions très oxidantes, acides et carbonatées. Ces solutions constitueraient donc une source possible de filons aurifères épigénétiques à des niveaux plus élevés des séquences de roches vertes. Quoique les réactions d'altération peuvent réduire la teneur en Ni de la minéralisation, l'augmentation volumique des sulfures représente peut-être le stade initial de la formation du minerai massif ferrifère dans les zones de métamorphisme dynamique intense.

(Traduit par la Rédaction)

INTRODUCTION

There are two major classes of ultramafic-associated Fe–Ni–Cu sulfide deposits in Western Australia. The ores providing the bulk of Ni production to date have been termed volcanic-associated deposits, and their characteristics are described by Groves et al. (1979). They are small lenses associated with thick peridotitic units interpreted to be basal flows within major sequences of peridotitic komatiite flows. Potentially more important, however, are larger deposits associated with intrusions of coarse-

FIG. 1. Geological sketch map of Eastern Gold-fields province, Yilgarn Block, showing locality of deposits referred to in text.

grained, close-packed dunites that are commonly semicontinuous along major lineaments over a strike length of up to 150 km (Binns et al. 1977): some bodies are smaller, discrete intrusions (e.g., Black Swan: Groves et al. 1974).

Although there is strong evidence for prior existence of magmatic sulfides in volcanic-associated deposits, these are strongly affected by regional amphibolite-facies metamorphism (Binns et al. 1976); the deposits are normally associated with thoroughly altered ultramafic rocks in which relict igneous mineralogy is rarely preserved (Barrett et al. 1977). In contrast, deposits in dunitic intrusions occur over a wide range of metamorphic environments, from greenschist to upper amphibolite facies. Most importantly, there are thick relict dunite pods in at least four localities that contain disseminated sulfides. Potentially these represent samples of original magmatic sulfides (Binns et al. 1977) with which sulfides from more thoroughly altered dunites can be compared, thus indicating the changes in ore mineralogy in response to conditions of metamorphic alteration (e.g., Eckstrand 1975), together with any redistribution of ore elements (cf., Binns et al. 1977) during alteration.

Platinum-group elements (PGE) seem to be immobile during alteration processes (e.g., Keays & Davison 1976), so that studies of their distribution relative to other ore elements are potentially very useful. Previous studies of the PGE content of disseminated mineralization in an altered dunitic intrusion at Black Swan (Keays et al., in press) indicate substantial redistribution of S, Au and Ni between serpentinites and talc–carbonate rocks or between silicate and sulfide phases (or both cases), but in this instance there are no relict sulfide-bearing dunites for comparison. The major object of the present study is to remedy this by examination of ore-element redistribution during progressive alteration of sulfide-bearing dunites from the Mt. Keith–Betheno area.

SETTING OF MT. KEITH-BETHENO MINERALIZATION

Regional setting

The dunite-associated mineralization in the Wiluna (Fig. 1). Dunite bodies are now normally with a discontinuous series of elongate, steeply dipping metamorphosed dunite pods occurring along a NNW-trending major lineament for ca. 150 km from south of Perseverance to north of Wiluna (Fig. 1). Dunite bodies are now normally

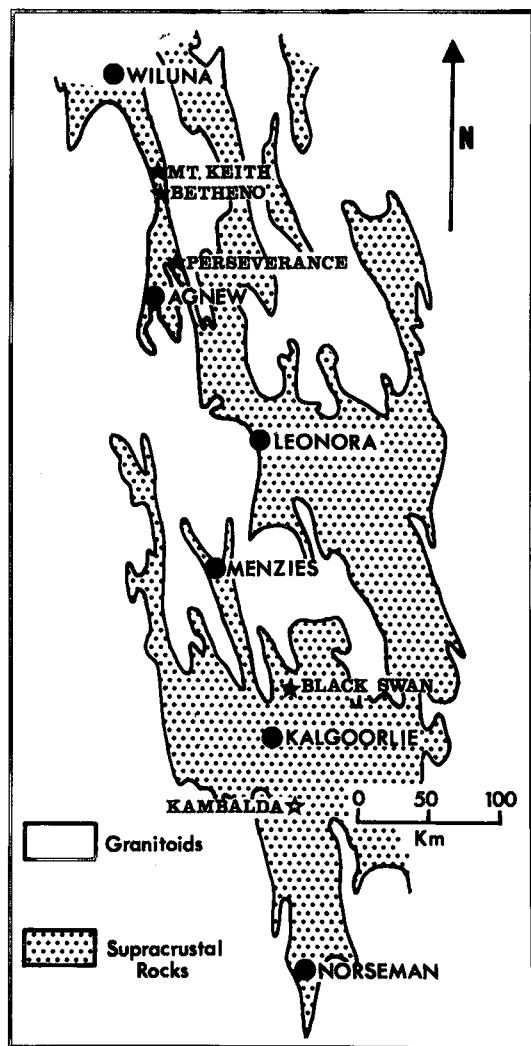concordant with country rocks, but are locally discordant. Marginal shearing and boudinage of the bodies during subsequent tectonism has obscured original relationships with country rocks in most cases. At Mt. Keith–Betheno, the dunite-associated deposits contrast with volcanic-asso- ciated deposits from other localities in that they are not, at least in their present position, specifically associated with ultramafic flow sequences; rather, the country rocks include felsic metavolcanic and metasedimentary rocks together with mafic and ultramafic rocks (Figs. 2, 3).
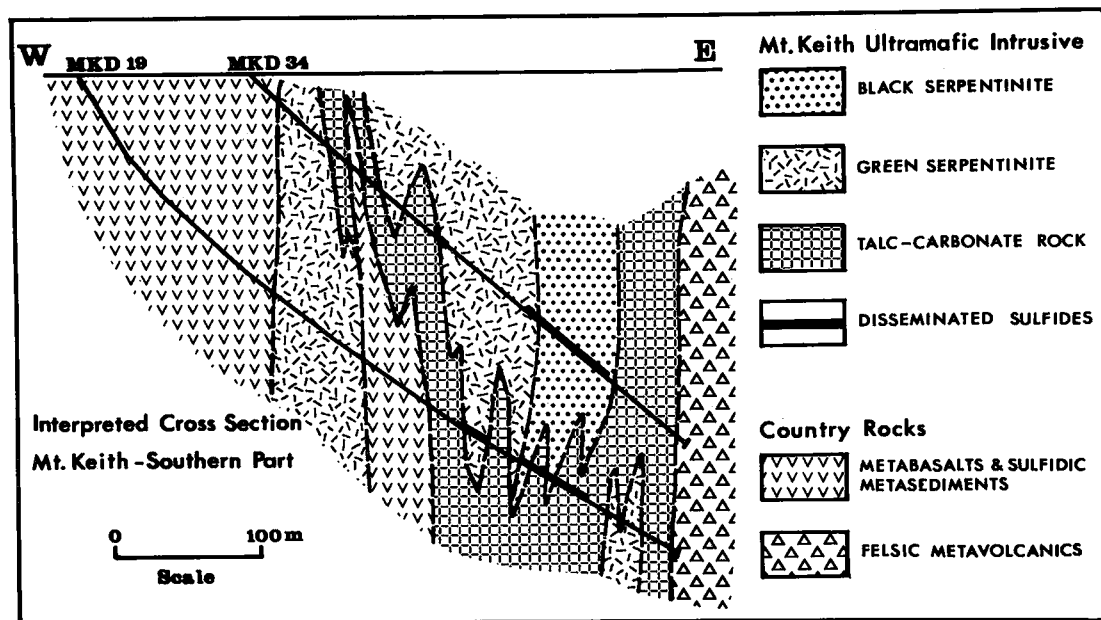

FIG. 2. Interpreted cross-section of the southern part of the Mt. Keith deposit, showing drillholes MKD19 and MKD34 (see Table 1). Section interpreted by R.J. Gunthorpe from drill-core data.
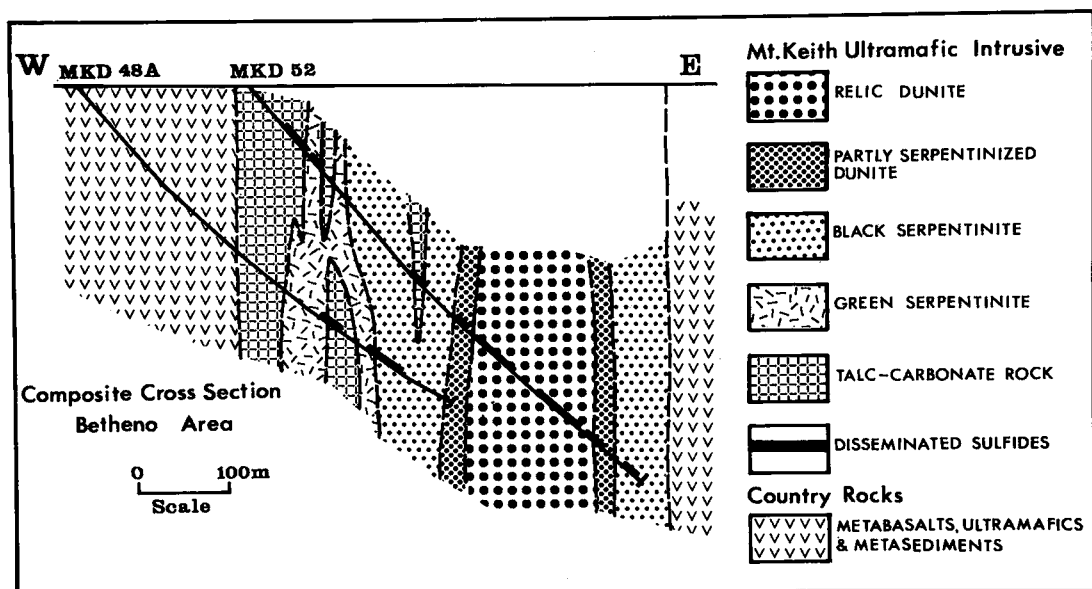

FIG. 3. Interpreted composite cross-section of Betheno area. Drillhole MKD48A projected into the line of section of drillhole MKD52. Section interpreted by R.J. Gunthorpe from drill-core data.

A genetic relationship between dunite pods and komatiitic volcanic rocks is not apparent in this area. Naldrett & Turner (1977), however, have presented evidence from Yakabindie, south of Betheno, that dunite pods are genetically related, and may represent subvolcanic feeders to spinifex-textured ultramafic flows in this area. Further clarification of relationships is required.

The belt of dunites transects the regional metamorphic isograds (Archibald *et al.* 1978) so that there is considerable mineralogical variation from lizardite serpentinites at Wiluna to olivine–talc metadunites at Perseverance (Fig. 1). There seems to be a *broad* geographic variation in degree of fractionation of the dunitic bodies and in the nature of contained mineralization that broadly parallels the variation in metamorphic grade. In very low-grade domains (*e.g.*, Wiluna) the dunites show marginal fractionation to orthopyroxenite, norite and sodic granophyre (R.J. Gunthorpe, unpubl. data, Univ. W. Aust.) and contain no mineralization; in intermediate environments (*e.g.*, Mt. Keith), the dunites have minor marginal orthopyroxenites [Naldrett & Turner (1977) record thicker marginal peridotites from "Six-mile" in the Yakabindie area] and contain disseminated sulfides, whereas in the higher grade domains (*e.g.*, Perseverance), dunites show no marginal fractionation and contain both disseminated and massive sulfides (*e.g.*, Martin & Allchurch 1975). These relationships could be simply explained in terms of increasing fractionation of a single or related series of ultramafic intrusions with increasing crustal level (*e.g.*, Binns *et al.* 1977), but information is patchy, field relationships unclear and the possibility of several periods of emplacement of ultramafic intrusions along this important crustal fracture zone cannot be ignored.

Mt. Keith deposit

The surface geology of Mt. Keith has been interpreted by Burt & Sheppy (1975) from suboutcrop and drillhole data. The dunite intrusion is up to 1,000 m thick and in the section chosen for examination (Fig. 2) is broadly zoned with a central core of black serpentinite partly surrounded by green serpentinite and a marginal zone of talc-carbonate rocks. Disseminated sulfides are mainly centrally disposed within black serpentinite but extend laterally or down-dip (or both) into green serpentinite and talc–carbonate rocks.

Country rocks include both tholeiitic and komatiitic metabasalts, felsic metavolcanic units, pelitic metasedimentary rocks and a continuous sulfide-rich metasediment horizon along the western contact of the dunite. Metamorphic assemblages (Barrett *et al.* 1977) are consistent with mid- to upper-greenschist facies, and preserved primary structures and textures indicate a low-strain environment.

Betheno deposit

At Betheno, approximately 15 km south of Mt. Keith, the dunite body is up to *ca.* 500 m thick and comprises a central core of preserved dunite which shows progressive serpentinization towards the margins and is enveloped by black serpentinite with marginal talc–carbonate rocks, together with some discrete zones of carbonation (Fig. 3). Disseminated sulfides occur in all lithologies. Country rocks are similar to those at Mt. Keith, but the assemblages indicate lowermost amphibolite-facies metamorphism (Barrett *et al.* 1977).

ALTERATION OF DUNITE

The following brief summary of the alteration sequence and mineralogies, broadly from the centre outwards, is largely taken from unpublished AMIRA (Australian Mineral Industries Research Association) reports at the University of Western Australia (UWA), prepared largely by R.J. Gunthorpe.

The relict dunite at Betheno consists of close-packed olivine grains (Fo_{92-94}) ranging from 3 mm to 2 cm across, with interstitial lobate chromite grains. The olivines, typically pale pinkish brown in color, contain numerous minute platelets of spinel similar to those produced experimentally during high-temperature oxidation of olivine (*e.g.*, Champness 1970, Pitt & Tozer 1970). They are interpreted to result from anhydrous reheating of original igneous olivines during lower-amphibolite-facies metamorphism, and differ from the elongate, colorless olivines associated with talc and produced by metamorphism of serpentinite (*e.g.*, Evans & Trommsdorff 1974).

The olivines have been variably serpentinized along grain margins, particularly towards the margins of the relict dunite pod. At Betheno, partly serpentinized dunites grade laterally into black serpentinite in which original olivine outlines are well preserved by serpentine containing abundant minute magnetite grains; interstitial areas (mesh lines) are marked by chlorite, stichtite after chromite, brucite and magnetite. The serpentine is largely lizardite, but recrystallization to antigorite has occurred adjacent to mesh lines and fracture surfaces. Black ser-

pentinites have similar bulk composition on a volatile-free basis to unserpentinized dunites (UWA, unpubl. analyses).

Green serpentinites are similar in texture to black serpentinites, but consist of colorless antigorite pseudomorphs after olivine and coarser grained magnetite aggregates. Their relationship to the black serpentinites is obscure. With increasing carbonation, both serpentine types grade into talc–magnesite rocks containing minor chlorite. Most green serpentinites and talc–magnesite rocks have volatile-free bulk
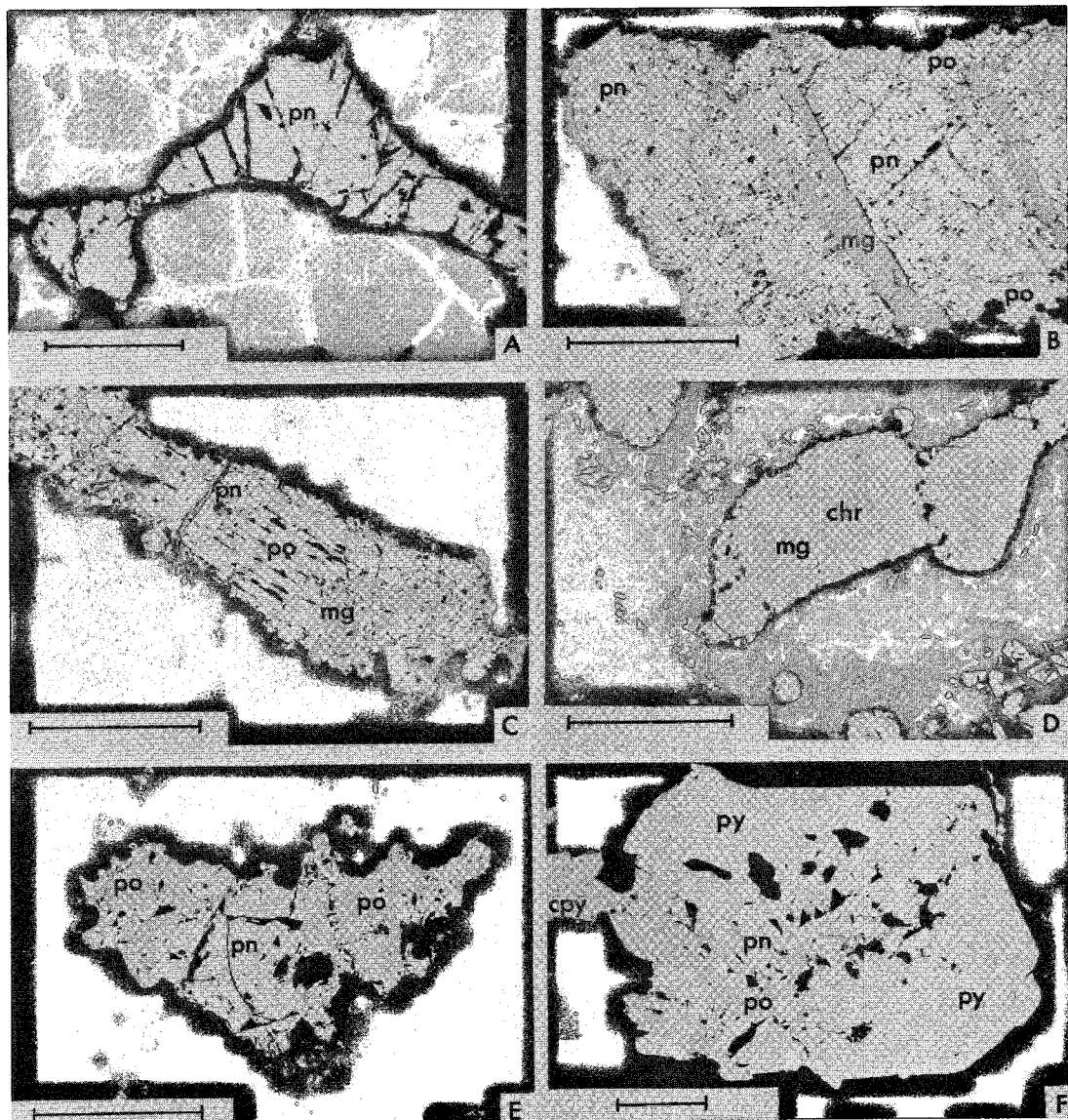

FIG. 4. Photomicrographs showing change in sulfide–oxide mineralogy and texture with progressive alteration. Scale bar 0.5 mm in length. A. Lobate pentlandite interstitial to olivine in relict dunite; MKD52/1612.5m. B. Magnetite and pyrrhotite veining and rimming pentlandite in black serpentinite; MKD48A/1549m. C. Irregular intergrowths of pyrrhotite, pentlandite and magnetite in black serpentinite; MKD48A/1501m. D. Valleriite replacing magnetite rims on chromite in black serpentinite; MKD48A/1475m. E. Recrystallized pyrrhotite–pentlandite aggregate (no magnetite) in carbonated green serpentinite; MKD48/1437m. F. Recrystallized pyrite–pentlandite–pyrrhotite–chalcopyrite aggregate in talc–carbonate rock; MKD19/1429m.

compositions similar to relict dunites and black serpentinites, although lower MgO contents characterize the margins of the body (UWA, unpubl. data); these have been avoided in sampling for this study. In most examples, the original texture of the dunite is destroyed, but in some cases mesh texture of precursor serpentinites is preserved.

SULFIDE MINERALIZATION

Sulfide mineralogy shows a sympathetic variation with the degree of hydration and carbonation of the dunite. The major mineralogical and textural features of sulfide–oxide aggregates are outlined below.

Sulfides in dunites

Lobate sulfide grains from *ca.* 0.1 to 1.0 mm in length occur interstitially to olivines within unserpentinized dunite at Betheno (Fig. 4A). They occupy similar textural positions to chromite, but are very rarely intergrown with that mineral. They are interpreted as intercumulus magmatic sulfides. In dunites with less than 10% serpentinization, the sulfide is exclusively pentlandite; pyrrhotite and magnetite are absent [*cf.*, Binns *et al.* (1977) for other examples at Perseverance and Forrestania].

The pentlandite in recrystallized dunites potentially represents the closest approximation to unmodified magmatic sulfide available in Western Australia. However, if pentlandite originally formed as the sole magmatic sulfide phase by reaction of monosulfide solid solution (MSS) and $(Ni,Fe)_3 \pm_x S_2$ below 610°C (*e.g.*, Kullerud 1963) it would have to form an initial liquid of pentlandite composition, which does not lie on any obvious liquid line of descent in experimental systems. It is more likely that subsolidus re-equilibration between olivine and MSS at high magmatic or metamorphic temperatures modified the compositions of original disseminated magmatic sulfide aggregates. However, there are problems in reconciling theoretical estimates of the compositions of sulfide liquids, estimates of possible subsolidus uptake of Ni in sulfides and the persistent occurrence of pentlandite over a wide range of sulfide concentration (0.5 to 6.0 wt. %) in relict dunite.

The composition of sulfide liquid coexisting with silicate liquid and olivine (Fe/Ni of *ca.* 15) can be deduced using olivine/silicate liquid and sulfide liquid/silicate liquid partition coefficients (*e.g.*, Duke & Naldrett 1978); such composition can be regarded as estimates only because experimentally determined partition coefficients must be extrapolated to the natural

situation involving higher MgO liquids and higher temperatures. Using Duke's & Naldrett's (1978) equations, the wt. % MgO in silicate liquid can be estimated to be *ca.* 30%, $K_{D(Ni-Fe)}^{O/L}$ 3.0 and $K_{D(Ni-Fe)}^{S/L}$ 21. This gives an Fe/Ni ratio of *ca.* 2.2 for sulfide liquid formed in equilibrium with silicate liquid from which the close-packed olivines of the dunite crystallized. This ratio contrasts with the Fe/Ni ratio of *ca.* 0.8 in the disseminated pentlandite.

Binns *et al.* (in prep.) show that in dunites with less than 0.1% S, most olivines contain $0.46 \pm 0.02\%$ NiO, whereas immediately adjacent dunites (*ca.* BJ cm away) with greater than 0.5% S have olivines with $0.33 \pm 0.03\%$ NiO. This may result from original magmatic heterogeneity, with equilibration on a fine scale between sulfide liquid, silicate liquid and olivine, or from subsequent subsolidus equilibration. If this variation were entirely due to redistribution of Ni between olivines and sulfides during subsolidus equilibration, the sulfides would be expected to be more Ni-rich than at present. For example, the expected increase of *ca.* 2% Ni in the sulfide fraction for a 5% sulfide concentration is greater than the present Ni content of such sulfide concentrations; this problem is compounded for the very low sulfide concentrations of some dunites; the expected increase in Ni concentration within the sulfide fraction with decreasing sulfide concentration is not observed. Moreover, the composition of MSS from which pentlandite could form purely by addition of Ni is limited to a composition with Fe/Ni only slightly higher than pentlandite (*i.e.*, *ca.* 1.0). These considerations, when constrained by the occurrence of pentlandite as the sole sulfide phase in dunites, irrespective of sulfide concentration, and by low Ni diffusion rates in olivine at subsolidus temperatures (*e.g.*, Clark & Long 1970), indicate that substantial modification of original magmatic sulfides by subsolidus Ni addition is unlikely, but this interpretation is in obvious conflict with the theoretically calculated sulfide-liquid composition. The high S/Se and Ni/Pd ratios of the sulfide fraction of the dunites relative to sulfides of the volcanic ultramafic association (*e.g.*, Kambalda) are rimmed by magnetite. Some Ni for forma- *and* S (from an external source) to a magmatic MSS (see below).

It must be concluded at this stage that the precise origin of the pentlandite in dunites is unclear; the problem may be resolved as more precise partition coefficients relevant to high-temperature magmas become available. In any case, pentlandite can confidently be considered

as the precursor to sulfide assemblages of similar concentration range now present in serpentinites and talc–carbonate rocks.

Partly serpentinized dunite

In incompletely serpentinized dunites at Betheno, interstitial pentlandite is progressively replaced by heazlewoodite and magnetite with increasing serpentinization, and chromite grains are rimmed by magnetite. Some Ni for formation of heazlewoodite may have come from pentlandite, as it is Ni-poor relative to that in unserpentinized dunites; the composition of pentlandite is not that which would normally be in equilibrium with heazlewoodite (Fig. 5). In addition, small (< 0.1 mm) grains of heazlewoodite and, much less commonly, awaruite occur along serpentine mesh-lines and more rarely within serpentine pseudomorphs after olivine.

Black serpentinite

The discontinuous nature of sulfides precludes observation of the transition in sulfide mineralogy from partly serpentinized dunite to black serpentinite. In some black serpentinites the opaque assemblage comprises interstitial pentlandite that is veined along cleavages by magnetite with minor marginal pyrrhotite (Fig. 4B), whereas in others pyrrhotite is a major phase occurring as irregular grains, together with pentlandite and magnetite (Fig. 4C). Pyrrhotite has replaced both pentlandite and magnetite and has grown along grain aggregate margins. In some cases, pyrrhotite grains connect pentlandite-dominated aggregates and lobate chromite grains. Composite aggregates are somewhat larger (up to 1.5 mm long) than those of the dunite. Pentlandite compositions (Fig. 5) are equivalent to those in other pyrrhotite-bearing assemblages that have equilibrated to low temperatures (cf., Misra & Fleet 1973). There is an antipathetic relationship between pyrrhotite and magnetite, as shown by the significant negative correlation (–0.65) between Fe/Ni ratio of sulfides (high Fe/Ni = high pyrrhotite content) and magnetite content for selective sulfide analyses (unpubl. UWA data).

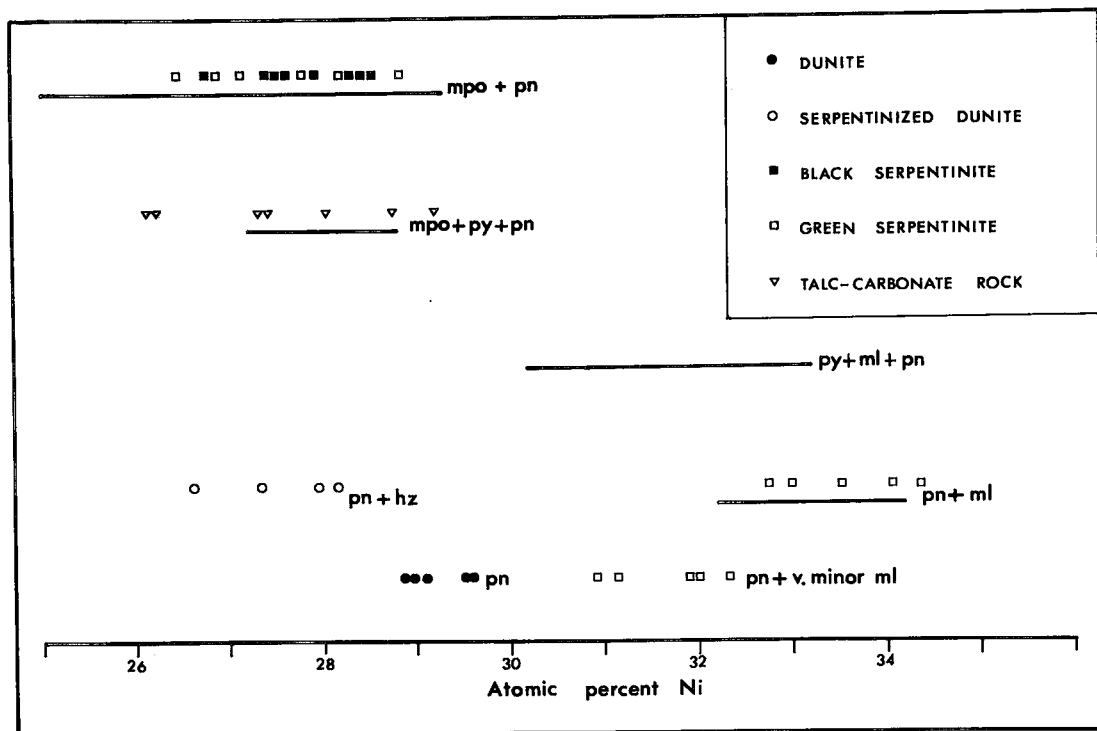An important additional phase is valleriite which rims composite magnetite–chromite grains

FIG. 5. Summary diagram showing compositional variation of pentlandite in different sulfide assemblages from dunites and altered dunites at Mt. Keith–Betheno. Pentlandite analyses by MAC 400S electron microprobe at 19.3 kV and 10-11μA specimen current at CSIRO Division of Mineralogy, Western Australia. Solid lines represent compositional variation of pentlandite in equilibrium with respective Fe–Ni sulfides from Misra & Fleet (1973).
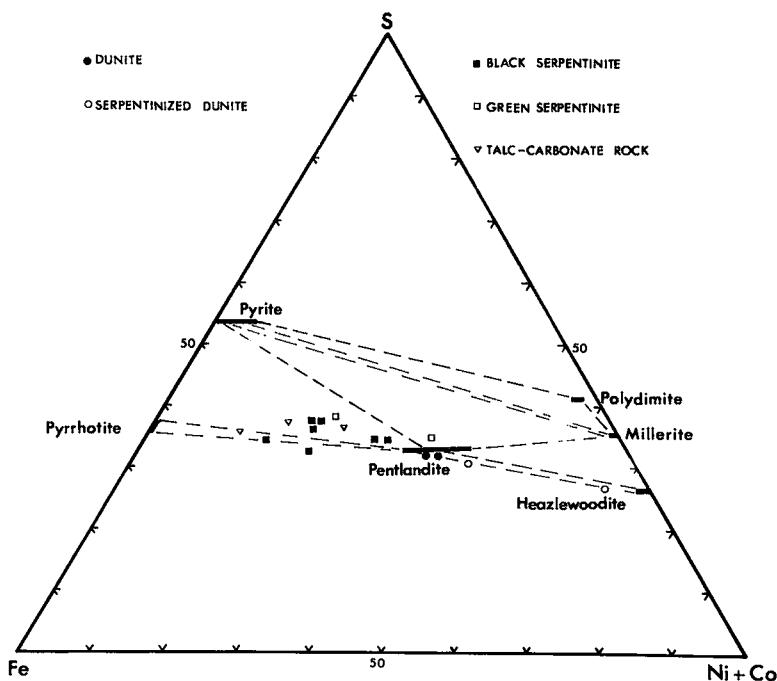
FIG. 6. Sulfide compositions from Mt. Keith–Betheno in terms of Fe–Ni+ Co–S. Bulk sulfide analyses determined by R.F. Lee using method of Davis (1972), and mineral compositions by electron microprobe as for Figure 5.

(Fig. 4D) and marginal magnetite in sulfide–magnetite aggregates (cf., Nickel & Hudson 1976) or occurs as veinlets along serpentine mesh-lines. It is most abundant in pyrrhotite-rich serpentinites. Chalcopyrite and gersdorffite are rare accessory phases. Sulfide aggregates are pervasively retextured in more antigorite-rich serpentinites.

The sulfide–oxide mineralogy of black serpentinites at Betheno and Mt. Keith is identical, thus allowing direct comparison of alteration types between the two areas, despite the small difference in peak metamorphic temperatures.

Green serpentinites

In green serpentinites, the most common aggregates consist of strongly recrystallized polygonal pyrrhotite grains intergrown with pentlandite (*e.g.,* Fig. 4E) with or without magnetite or chalcopyrite. Pentlandite has a similar composition to that in black serpentinites (Fig. 5). Valleriite is normally absent. In a few specimens, the assemblage millerite–Ni-rich pentlandite (Fig. 5)–magnetite is present.

Talc–carbonate rocks

Sulfide assemblages in talc-carbonate rocks

are all strongly recrystallized and, in some cases, sulfides are replaced by carbonate. The most common assemblage is pyrite–pentlandite–pyrrhotite–chalcopyrite (Figs. 4F, 5), but gersdorffite is locally abundant and magnetite is rare. In some specimens, the assemblages millerite–magnetite and millerite–polydymite–pyrite (Fig. 6) are present. The rare occurrence of minute chalcopyrite grains as haloes around chromite grains suggests that they formed by *in situ* breakdown of valleriite during carbonation.

CONDITIONS OF ALTERATION

Spatial and textural relationships within the altered dunite suggest that the observed broadly zoned alteration sequence resulted from interaction of aqueous, carbonate-bearing solutions with dunite along a front towards the core of the intrusion; a hydration front preceded carbonation. Irregular fracture zones, providing localized ready access of solutions, probably controlled the formation of more limited talc–carbonate zones interspersed with serpentinite (*cf.,* Naldrett & Turner 1978). The fluid was probably metamorphic in origin and was derived from,

or previously interacted with, the surrounding sedimentary and volcanic rocks (*cf.*, Barnes & O'Neil 1976).

Although the nature of the initial alteration fluids cannot be precisely defined, they are considered by analogy with most natural waters to have been slightly oxidizing, near-neutral carbonated solutions (*cf.*, Barnes & O'Neil 1976). As discussed by Keays *et al.* (1979), initial serpentinization reactions involving hydrolysis of olivine would have made solutions highly alkaline, but the decreased ability of the rocks to raise the pH of incoming fluids as the two approach equilibrium would require that fluids would be only moderately alkaline during the end stages of serpentinization (*cf.*, Barnes *et al.* 1967). During initial carbonation, solutions would have been moderately alkaline, but with complete conversion to talc–magnesite assemblages, they would have remained carbonated and neutral.
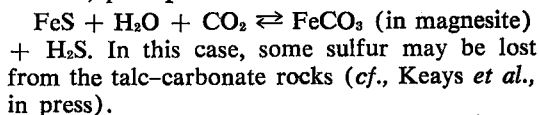
The variation in sulfide–oxide mineralogy throughout the altered dunite is broadly consistent with a control by Fe-related redox mechanisms as suggested by Eckstrand (1975). The occurrence of the assemblage pentlandite–heazlewoodite–magnetite ± very minor awaruite in partly serpentinized dunites indicates moderately reducing conditions (*cf.*, Eckstrand 1975). It is consistent with the reaction of anhydrous olivine containing Fe^{2+} with water to produce magnetite, thus lowering the redox state of the water. The change from a pentlandite–heazlewoodite–magnetite assemblage to a pyrrhotite–pentlandite–magnetite assemblage in black serpentinites cannot be simply attributed to a greater concentration of sulfides in the latter as there are equally high proportions of sulfides in some partly serpentinized dunites. The replacement of magnetite by pyrrhotite is consistent with a decrease in $f(O_2)$ and an increase in $f(S_2)$ in alteration fluids (Eckstrand 1975, Fig. 9), particularly as there is strong evidence for addition of sulfur during serpentinization (see below).

The opaque assemblages in talc–carbonate rocks are clearly the most oxidized, with pyrite–pyrrhotite–pentlandite the dominant assemblage. Rare pyrite–millerite–polydymite or disseminated millerite–magnetite assemblages indicate localized very oxidizing conditions similar to those at Black Swan (*e.g.*, Groves *et al.* 1974, Keays *et al.*, in press). As suggested by Eckstrand (1975), the oxidizing conditions result at least in part from incorporation of iron from breakdown of magnetite into magnesite with consequent addition of O_2 to the alteration fluid

according to the partial reaction:

$$Fe_3O_4 + 3CO_2 \rightleftarrows 3FeCO_3 + \tfrac{1}{2}O_2$$
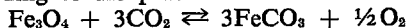
Textural evidence suggests some replacement of sulfides, perhaps *via* a reaction such as:

$FeS + H_2O + CO_2 \rightleftarrows FeCO_3$ (in magnesite) $+ H_2S$. In this case, some sulfur may be lost from the talc–carbonate rocks (*cf.*, Keays *et al.*, in press).

Apart from these indications that sulfide mineralogy is effectively buffered by reactions occurring in the dominant silicate (± carbonate) portion of the total rock system, there are several indications of redistribution of ore-forming elements during alteration processes. Relative to sulfide assemblages in unserpentinized dunite, major changes in composition of sulfide aggregates in altered rocks include marked increase in Ni/Fe and Ni/S ratios in partly serpentinized dunites and marked decrease in Ni/Fe and (Fe+Ni)/S ratios in serpentinites and talc–carbonate rocks (Table 1, Fig. 6), Furthermore, there is textural evidence of replacement of oxides (magnetite and chromite) by sulfides (pyrrhotite and valleriite) during serpentinization. In order to test whether these changes result from internal isochemical readjustment or from addition of components (*e.g.*, S) from an external source during alteration, as suggested by Binns *et al.* (1977), a study of PGE distribution and of S/Se ratios was carried out.

PLATINUM-GROUP-ELEMENT DISTRIBUTION

Analytical procedure

The majority of samples analyzed consisted of short (5 cm) pieces of drill core, but one large black serpentinite sample and three composite ore samples from the Mt. Keith winze were also analyzed. The samples were carefully cleaned with a sand (Al_2O_3) blaster and crushed in a soft iron mill known to have low precious-metal contents. Au, Ir, Pd, Co, Cr and Se were determined by a neutron-activation-analysis procedure modified from Crocket *et al.* (1968) and Keays *et al.* (1974). The accuracy of the method is estimated to be ± 15% (see Shaw *et al.* 1976). Copper and Ni were measured by atomic absorption spectrometry using a Varian Techtron Model AA–3 with a 1M–6D Indicator Module. Sulfur was determined with a Leco automatic S titrator.

Geochemistry : results

Analytical results are tabulated in Table 1 and plotted in Figures 7 to 11. Gold and S

TABLE 1. ANALYTICAL DATA AND ELEMENT RATIOS FOR DUNITES AND ALTERED DUNITES, MT. KEITH-BETHENO

Rock Type	Drill hole-feet	Pd ppb	Au ppb	Ir ppb	Ni ppm	Cu ppm	Co ppm	Cr ppm	S ppm	Se ppm	Pd/Ir	Ni/Co	Ni/Cu	Pd/Se	S/Se	Mineralization - Mineralogy
Dunite	MKD52-1524	65.0	0.70	12.2	11800	42	172	970	6610	0.518	5.3	69	280	125	12800	dissem. pn
"	MKD52-1596	79.0	9.90	18.6	14200	154	174	1150	9890	0.611	4.2	82	92	129	16200	dissem. pn
"	MKD52-1699	0.08	0.57	10.7	3700	3	104	1080	140	0.015	--	36	1233	5	9300	very dissem. hz+mag
Serpentinized dunite	MKD52-666	34.8	0.54	23.3	9230	190	309	832	4990	--	1.5	30	49	-	-	dissem. pn-mag-hz
"	MKD52-1268	114.0	7.95	18.2	18700	316	208	1020	13500	--	6.3	90	59	-	-	dissem. pn-mag-hz
"	MKD52-1292.5	137.0	4.08	27.4	12400	152	191	1280	9000	0.661	5.0	65	82	207	13600	dissem. pn-mag-hz
"	MKD52-1577	65.1	0.73	10.5	11600	63	140	568	9570	--	6.2	83	184	-	-	dissem. mag-hz-pn
Black Serpentinite	MKD19-1381	95.8	1.88	12.6	9800	254	217	792	10500	0.707	7.6	45	39	135	14800	dissem. pn-mag+minor vl-po
"	MKD19-1394	60.6	2.88	11.4	7500	611	166	907	8400	0.622	5.3	45	12	97	13500	dissem. pn-mag+minor vl-po
"	MKD19-1461	34.0	2.51	4.9	6280	297	169	853	17000	0.551	6.9	37	21	62	30050	dissem. po-pn-mag-cpy-gd.
"	MKD34-942	61.9	2.41	12.1	7950	194	189	754	8200	0.532	5.1	42	41	116	15400	dissem. pn-mag+minor vl-po
"	MKD34-991	38.1	17.70	10.1	6890	258	133	915	9600	0.531	3.8	52	27	72	18100	dissem. pn-mag-po
"	MKD34-1032	40.9	7.27	8.4	7160	266	166	948	11500	--	4.9	43	27	-	-	dissem. pn-mag-po
"	Winze specimen	63.9	2.32	16.1	7690	172	245	1050	15900	0.545	4.0	31	46	117	29200	dissem. po-mag-pn-vl
Green Serpentinite	MKD19-958	2.3	0.22	4.9	2000	30	72	1490	1720	0.143	0.5	28	67	16	12000	very dissem. po-pn+minor mag-cpy
"	MKD34-1063	36.4	0.99	7.1	6910	94	160	948	7720	--	5.1	43	74	-	-	dissem. po-pn-mag-cpy
"	MKD34-1173	12.9	1.44	6.1	3970	22	115	746	3090	--	2.1	35	178	-	-	dissem. po-pn-mag-cpy
Talc-carbonate rock	MKD19-1220	90.0	2.03	10.4	6890	39	158	1020	11300	0.582	8.6	43	176	160	19400	dissem. po-pn-py-cpy
"	MKD19-1429	61.3	3.07	5.8	5770	274	132	772	15700	0.674	10.6	44	21	91	22300	dissem. po-pn-py-cpy-gd
"	MKD19-1436	16.7	2.69	3.7	3400	159	85	727	11100	0.254	4.5	40	21	66	43700	dissem. po-pn-py-cpy-gd
"	MKD19-1498	87.6	6.82	19.1	8230	105	156	1000	11000	0.652	4.6	53	78	140	16900	dissem. py-pn-po-cpy
"	MKD19-1735	1.1	6.68	11.7	2500	5	96	1160	450	0.004	0.09	26	500	276	10500	very dissem. ml-mag
"	MKD34-1241	11.2	0.95	9.1	3410	21	85	567	2960	--	1.2	40	162	-	-	dissem. po-py
"	MKD48A-1245	51.6	2.10	13.8	7890	192	636	5320	9870	0.431	3.7	12	41	119	22900	dissem. po-pn-cpy
Composite sample	53958*	43.0	1.80	5.4	6000	20	--	--	6500	--	8.0	--	300	-	-	dissem. po-pn-mag
"	AA011301*	54.0	8.50	10.0	7550	190	--	--	13000	--	5.4	--	30	-	-	dissem. po-pn-mag
"	Composite*	47.7	12.00	20.3	7150	150	--	--	--	--	2.4	--	48	-	-	dissem. po-pn-mag

*University of Melbourne specimens. Abbreviations: cpy = chalcopyrite, gd = gersdorffite, hz = heazlewoodite, mag = magnetite, pn = pentlandite, po = pyrrhotite, py = pyrite, vl = vallerite.

have been plotted against Pd rather than Ni or Ir, present both in sulfide and silicate phases. This is shown in Table 1 where samples with low S contents have very low Pd/Ir ratios, and in Figure 7 where Pd contents below *ca.* 20 ppb are highly variable for relatively constant Ni. Although there is some scatter, there is no significant difference in Pd/Ir ratios between rock types, indicating that there is no consistent redistribution of these elements during alteration. A problem with interpretation is the relatively small range of PGE contents for rocks with significant sulfides because the concentration of the latter shows a restricted range (highest S content is 1.7%).

A plot of total Ni against Pd (Fig. 7) indicates an overall positive correlation but a scatter for samples with significant sulfide contents (*cf.*, Black Swan). In detail, the data define tight fields, with the dunites and serpentinized dunites having high Ni/Pd ratios relative to the serpentinites (including the composite samples which are mainly serpentine) and the talc–carbonate samples. The Ni/Pd ratios of the dunites and serpentinized dunites (average = 1.4 x 10^5) are double those of sulfide ores of the Kambalda type, which have Ni/Pd ratios averaging 0.73 x 10^5 (Ross & Keays 1979) whereas the serpentinites have ratios (average = 0.94 x 10^5) half-way in between. This suggests that Ni was added to sulfides in the dunites (and to the serpentinites prior to serpentinization), whereas the steep slopes of each of the fields in Figure 7 suggest that Ni addition was greatest for the least mineralized samples. The source of this Ni may have been the serpentinites. The significantly lower total Ni content of unmineralized ser-

pentinite (MKD 19/958 m = 2000 ppm Ni whereas assay data for unmineralized serpentinites indicate values of *ca.* 2500 ppm Ni)
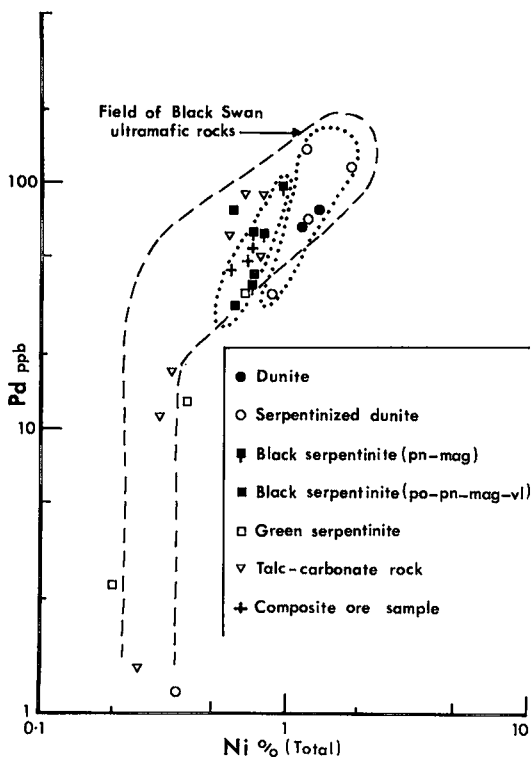

FIG. 7. Plot of total Ni(%) *versus* Pd (ppb) for variously altered dunites from Mt. Keith-Betheno. The dotted areas distinguish samples of dunites and serpentinized dunites from serpentinites. Field of Black Swan mineralized ultramafic rocks from Keays *et al.* (1979).
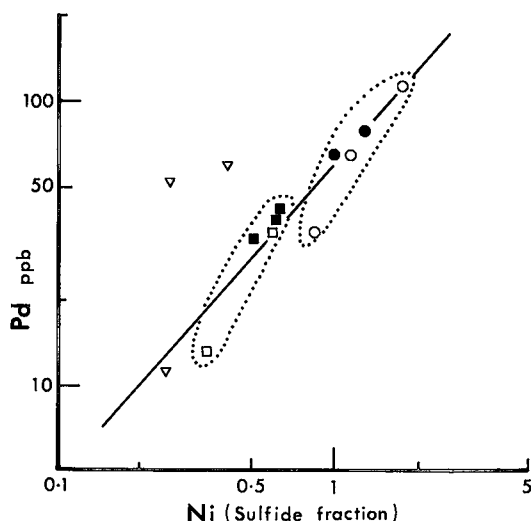
FIG. 8. Plot of percent sulfide Ni (bromine leach) *versus* Pd (ppb) for variously altered dunites from Mt. Keith–Betheno. The dotted areas as in Figure 7. Fewer samples have been analyzed than plotted on Figure 7.

relative to unmineralized dunites (MKD 52/ 1699 m = 3700 ppm Ni, approximately equivalent to microprobe analyses of olivine) suggests that even if allowance is made for specific gravity changes, some Ni was lost from the silicate phases during serpentinization. A plot of sulfide Ni against Pd (Fig. 8) for some of
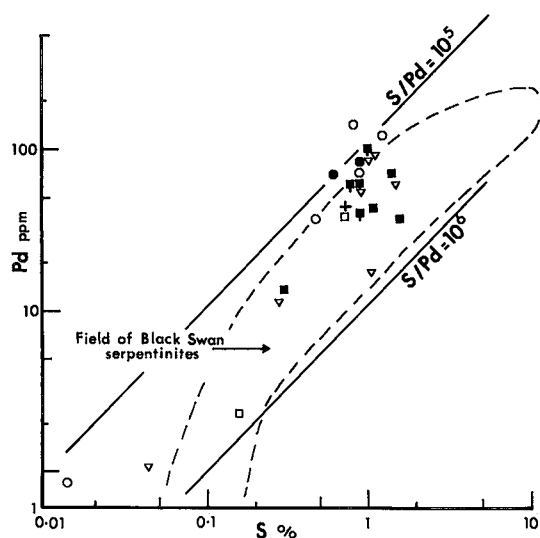

FIG. 9. Plot of S(%) versus Pd (ppb) for variously altered dunites from Mt. Keith-Betheno. Field of Black Swan serpentinites from Keays *et al.* (1979) is shown for comparison.

the samples indicates that Ni released from the silicates was not taken up by the sulfides, as these would then have had Ni/Pd ratios larger than those of sulfides in the dunites. Hence, the Ni liberated from olivine during serpentinization either left the system entirely or was added to sulfides in the dunites. It is perhaps significant that the difference in silicate Ni between the dunites and serpentinites accounts for the bulk of the displacement between the two fields shown in Figure 7. The data for talc–carbonate rocks (Figs. 7 and 8) suggest loss of Ni, at least in some samples, from both the sulfide and rock fractions.

Our interpretation can at best be considered tentative because of the lack of data and the possibility that we are dealing with magmatic heterogeneities. The dunites and serpentinized dunites all come from the Betheno area whereas the serpentinites and talc–carbonate samples come from the Mt. Keith area. The dunite preserved at Betheno may have had an initially higher Ni content than the ultramafic rock at Mt. Keith, as reflected in its higher Ni/Pd ratio.

Figure 9 indicates a very narrow range of S/Pd ratios for dunites, partly serpentinized dunites and black serpentinites in which pentlandite remains the dominant sulfide phase. Some talc–carbonate rocks overlap this range. Other serpentinites containing pyrrhotite and valleriite-rich assemblages and other talc–carbonate rocks have variable, but commonly higher, S/Pd ratios with a range similar to that of Black Swan serpentinites. Assuming that Pd has remained immobile, these data suggest addition of S to some sulfide assemblages during serpentinization. Low S/Pd ratios in talc–carbonate rocks may be directly inherited from serpentinites to which there was limited S addition; more likely, these are due to S loss from serpentinites with higher S/Pd ratios during carbonation (*cf.*, Keays *et al.*, in press).

A S-Se plot of fewer samples (Fig. 10) again indicates a close grouping of dunites, partly serpentinized dunites and black serpentinites containing pentlandite (range *ca.* 12,000 to 18,000 for significant sulfides, Table 1) along the low S/Se margin of the Black Swan serpentinite field. The ratios are only slightly higher than the mean ratio of 9,430 ± 1,870 (11 samples) obtained by Hughes & Keays (in prep.) for Kambalda ores, using neutron activation analysis for Se. Comparison is made with these ratios rather than the lower ratios quoted by Binns *et al.* (1977), using the technique of Michael & White (1976), so that all compared
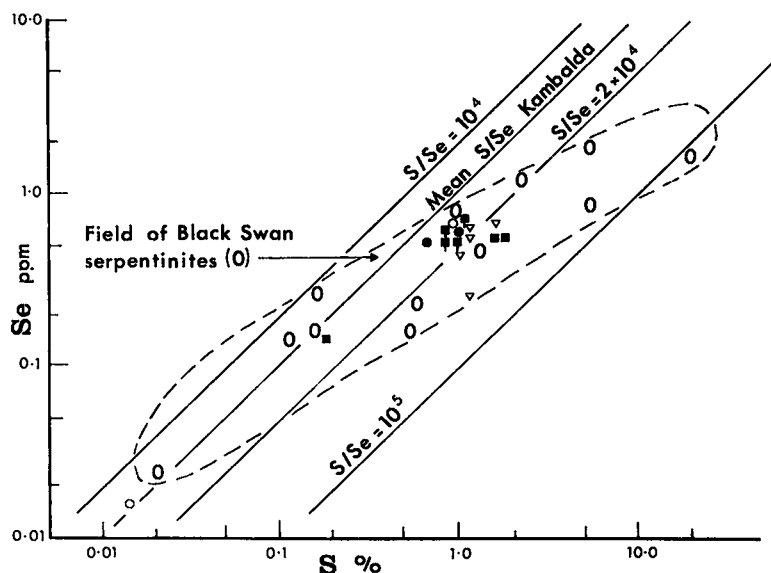
FIG. 10. Plot of S (%) *versus* Se (ppm) for variously altered dunites from Mt. Keith–Betheno compared to Black Swan serpentinites (Keays *et al.* 1979).

data are derived from a constant source and similar analytical method; the conclusion is unaltered whichever internally consistent set of data is used. If the difference between the mean and S/Se ratios of the Kambalda ores and the pyrrhotite-free Mt. Keith rocks is real, it suggests that some S was added to the latter prior to serpentinization. There is a wide scatter of S/Se ratios for other Mt. Keith serpentinites and talc–carbonate rocks (range *ca.* 17,000 to 44,000). Although data points are clustered, there is a broad trend towards higher S/Se (relatively constant Se) with increasing S content as at Black Swan (Keays *et al.,* in press).

A Au-Pd plot (Fig. 11) reveals a wide scatter of data points, with even the two unserpentinized dunite samples that otherwise show consistent relationships showing extreme variation. There is no distinction between talc–carbonate rocks and serpentinites as at Black Swan (Keays *et al.* 1979).

ELEMENT REDISTRIBUTION DURING ALTERATION

Original magmatic component

The PGE data, in particular the relatively narrow ranges of Ni/Co, Pd/Ir and Pd/Se (Table 1), add to the textural and mineralogical evidence for the existence of magmatic sulfides

in dunites and variously altered equivalents. The mean Pd/Ir ratio of 5.4 for samples with significant sulfides is close to the ratio of 6.2 for Kambalda ores (Keays & Davison 1976).
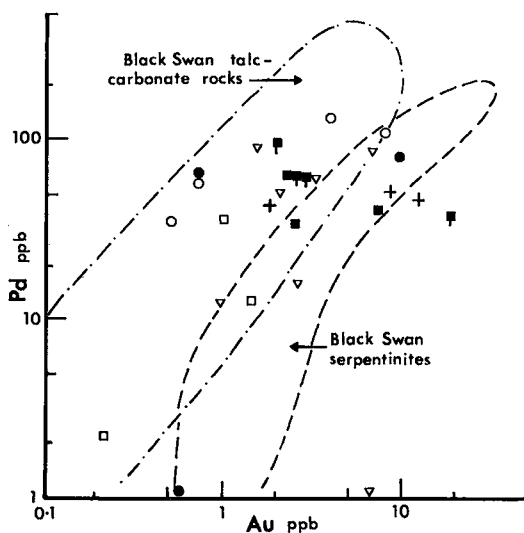

FIG. 11. Plot of Au (ppb) versus Pd (ppb) for variously altered dunites from Mt. Keith–Betheno. Fields for Black Swan serpentinites and talc–carbonate rocks from Keays *et al.* (1979) are shown for comparison.

Addition of sulfur and probable loss of nickel

Although data for Ni and S as a function of Pd in dunites and partly serpentinized dunites are few, they suggest that these elements were redistributed internally during initial serpentinization. Nickel loss from the serpentinized olivines was presumably balanced by the generation of additional, minute sulfide grains (heazlewoodite) within serpentine. The much greater volume of the lobate sulfide aggregates than the smaller disseminated grains, combined with the probable internal conservation of Ni and S, requires that magnetite was largely added to the lobate aggregates and did *not* replace pentlandite *via* a reaction such as $Fe_9Ni_9S_{16} + 6O_2 \rightleftarrows 3Fe_3O_4 + 3Ni_3S_2 + 5S_2$ thus suggesting a dilational origin for magnetite veins along pentlandite cleavages (Fig. 4B). This type of internal distribution is essentially similar to that described by Eckstrand (1975) from Dumont, involving an increase in the Ni tenor of sulfide aggregates, but no overall increase in total Ni.

With progressive serpentinization, more Fe- and S-rich sulfide aggregates were developed by a combination of significant S gain and probable slight Ni loss, as indicated by S–Pd and Ni–Pd relationships, and Fe gain as demanded by sulfide compositions and concentration levels. However, the addition of S during serpentinization was not as pervasive as at Black Swan (Keays *et al.* 1979). The S–Se relationships are also consistent with S gain during serpentinization. As Se would have behaved as an inert species under the reducing conditions imposed by active serpentinization (Yamamoto 1976), the increase in S/Se with increasing S content is best explained by an increase in S from an external source. Potential sources for this S are sulfide-rich metasediments in the country-rock sequences at Mt. Keith. These have higher S/Se ratios than the dunites (mean *ca.* 38,000 for unpublished analyses using the method of Michael & White 1976); any solutions transporting S as a reduced species (H_2S, HS^- or S^{2-}) would have had significantly lower ratios than this (Yamamoto 1976). Therefore, new sulfides formed from an external source, such as S-rich metasediments, should have very high S–Se ratios so that combinations of magmatic sulfides and newly formed sulfides should show almost constant Se with increasing S (*cf.*, Fig. 10).

Reconnaissance sulfur istotope data (Donnelly *et al.* 1978) for Mt. Keith sulfides indicate slightly negative $\delta^{34}S$ values, in contrast to slightly positive $\delta^{34}S$ values for most volcanic-associated ores (*e.g.*, Kambalda) and for most magmatic sulfides. These negative values are consistent with fractionation of sulfur isotopes by either hydrothermal transport of sulfur in solutions containing both oxidized and reduced species at some stage(s) or with derivation of the sulfur from a source with negative $\delta^{34}S$ values, for example sulfide-rich sediments formed in environments where isotopic fractionation was possible (Groves *et al.* 1979). They are therefore consistent with our other geochemical evidence of sulfur addition.

Textural relationships in black serpentinites suggest that the additional sulfide was pyrrhotite that precipitated largely at sites of pre-existing magmatic sulfide aggregates. There is no direct evidence that these sulfides underwent a previous alteration to heazlewoodite, but rather that there was direct addition to, or replacement of, pentlandite–magnetite aggregates (Figs, 4B, C). The ubiquitous presence of valleriite along mesh lines, around spinel grains and around sulfide aggregates, coupled with indications that the lobate sulfide aggregates became more S-rich, suggests that these also represent the depositional sites of introduced S. Textural evidence for S addition is obscured by recrystallization in green serpentinites, presumably due to rapid diffusion of Fe and Ni within the sulfide aggregates (*e.g.*, Klotsman *et al.* 1963, Condit *et al.* 1974).

The formation of additional sulfides at Black Swan has previously been discussed by Keays *et al.* (1979), and a similar mechanism appears applicable at Mt. Keith. Precipitation probably occurred because of the development of Eh gradients across mesh lines in which most pre-existing sulfides were located during progressive serpentinization. More oxidizing conditions along mesh lines, due to completion of serpentinization reactions and influx of new fluids, would promote precipitation of sulfides *via* reactions such as: $\frac{1}{2}O_2 + 2H_2S + Fe^{2+} \rightleftarrows 2FeS + 2H^+ + H_2O$. Magnetite may form if conditions were sufficiently oxidizing or be consumed if they were more reducing. The high percentage of Fe sulfides resulted from greater availability of Fe from silicate phases and the greater mobility of Fe^{2+} compared to Ni^{2+} (NiS has a much smaller solubility product than FeS).

Complete serpentinization at Mt. Keith thus increased the total volume of sulfides, but did not produce an increase in Ni tenor of mineralization. Data from talc–carbonate rocks suggest that no S was added, but that sulfide-oxide aggregates recrystallized under conditions of higher $f(O_2)$ and $f(S_2)$ to the present S-rich

assemblages, with loss of Ni in at least some assemblages. Some S loss possibly occurred during carbonation, but it was not pervasive as at Black Swan (Keays *et al.* 1979).

Although alteration reactions have not upgraded Ni mineralization at Mt. Keith–Betheno, the resultant increase in sulfide volume may be a critical step towards production of more massive ores within dunitic intrusions in higher grade metamorphic environments of higher strain (*e.g.,* Perseverance, Forrestania: Binns *et al.* 1977). Several geochemical parameters (Binns *et al.* 1977), including high Fe/Ni ratios (mean *ca.* 2.9 for strongly disseminated ores and 6.0 for massive ores), high S/(Fe+Ni) ratios (mean *ca.* 1.2 for strongly disseminated ores and 1.35 for massive ores) and high S/Se ratios (mean *ca.* 27,000 for strongly disseminated ores and 42,000 for massive ores, using the method of Michael & White 1976) suggest the possibility that the ores in dunites from higher grade environments formed by metamorphic upgrading of sulfides that had been significantly modified by alteration reactions such as those described above. The Fe/Ni ratios are even higher than ratios for volcanic-associated ores (Groves *et al.* 1979); they and the very high S/Se ratios seem incompatible with an origin involving direct settling of magmatic sulfide-oxide liquids that equilibrated with highly magnesian silicate liquids (*cf.,* Duke & Naldrett 1978).

Redistribution of gold, copper and arsenic

The Au–Pd plot (Fig. 11) indicates an erratic distribution of Au in all ultramafic lithologies. Data from dunites and serpentinized dunites that contain pentlandite as the dominant sulfide phase show the widest spread of Au relative to Pd in contrast to their very narrow range in terms of other components. Either Au was initially irregularly distributed or alteration resulted in localized dissolution and transport of Au to produce the heterogeneous distribution. The Mt. Keith data contrast markedly with those from Black Swan (Fig. 11). It seems most likely that the behavior of Au in the alteration environment is strongly dependent on $f(O_2)$ of alteration fluids, with dissolution and removal of Au from ultramafic rocks enhanced by strongly oxidizing conditions as at Black Swan.

The Ni/Cu ratios of all mineralized rocks and sulfide fractions (unpubl. data) are significantly higher than those for all other nickel sulfide ores, in agreement with their highly magnesian host rocks (*cf.,* Rajamani & Nladrett

1978). Ni/Cu ratios for dunites and partly serpentinized dunites from Table 1 (mean 124, standard deviation 90) are higher than those serpentinites and between 60 and 1,400 for 56, st. dev. 73) but there is considerable scatter; part of this variation may be related to Ni loss during progressive alteration. Further, there is a complete overlap of all lithologies in terms of Cu–Pd (not plotted). Hence, there is no conclusive evidence of Cu addition during alteration. The small concentration of Cu in dunites is largely present in pentlandite, whereas comparison of total Cu *versus* sulfide-leach Cu values indicate that Cu is largely present in valleriite in serpentinites. The lower Ni/Cu ratios of sulfide-leach solutions for talc–carbonate rocks relative to serpentinites confirm that Cu is present in ubiquitous chalcopyrite.

Unpublished As data (using the method of Michael 1977) from Mt. Keith–Betheno indicate ranges of S/As ratios between 2,700 and 22,500 for dunites, between 50 and 75,000 for serpentinites and between 60 and 1,400 for talc–carbonate rocks. The erratic distribution of As is consistent with the sporadic occurrence of gersdorffite, the only As-rich mineral observed during this study of the sulfide assemblages. The very low S/As ratio of talc–carbonate rocks and some serpentinites suggests introduction of As in alteration fluids, particularly in those enriched in carbonate. The common occurrence of significant arsenides and sulfarsenides in talc–carbonated sulfide ores (*e.g.,* Spargoville, Redross) and their relative rarity in ores within serpentinite host rocks elsewhere in Western Australia supports this contention.

SUMMARY AND CONCLUSIONS

Intrusive dunite bodies occurring either singly or along linear belts up to 150 km in length represent important hosts to nickel mineralization in Western Australia. In lower grade metamorphic domains that we have studied they were normally completely altered during metamorphism by fluids that progressed from the country rocks along a broad front towards the core of the intrusions with more local introduction of fluids along fracture zones. Conditions changed from highly alkaline and reducing during initial serpentinization to neutral and relatively oxidizing during carbonation.

In several localities, including Betheno, the altered dunites have a core of recrystallized, but otherwise unaltered, dunite that contains disseminated pentlandite. At Betheno, the composition of the initial phase to crystallize from

intercumulus magmatic sulfide liquid is debatable. The occurrence of pentlandite alone in dunites with 0.5 to 6.0 wt. % sulfides suggests little subsolidus modification of precursor phases, but theoretical estimates of sulfide-liquid composition indicate Fe/Ni ratios of *ca.* 2.1 rather than *ca.* 0.8 of the pentlandite or *ca.* 1.0 of MSS from which pentlandite could form by Ni addition alone. Whatever its origin, the pentlandite clearly represents a pre-alteration sulfide composition with which assemblages in altered rocks can be compared.

Textures and mineralogy of sulfides in the zoned alteration sequence at Mt. Keith–Betheno (and Black Swan) indicate that sulfide assemblages are broadly controlled by Fe-related redox mechanisms as suggested by Eckstrand (1975), so that sulfide mineralogy for a given bulk composition varies sympathetically with alteration type. However, at Mt. Keith–Betheno there is also a systematic change in bulk sulfide composition, with serpentinites and talc–carbonate rocks having much higher Fe/Ni ratios than dunites and partly serpentinized dunites which have very low Fe/Ni ratios. A study of Ni, Cu, Au, Se, S and As distribution with respect to the presumed immobile elements Pd and Ir leads to the following conclusions regarding redistribution of ore elements:

1) There were magmatic sulfide concentrations at the sites of present mineralization prior to alteration of the dunite; a similar conclusion is reached at Black Swan (Keays *et al.* 1979).

2) There was an approximation to internal conservation of ore elements, with the possible exception of Au, during partial serpentinization of dunite that resulted in the assemblage heazlewoodite–pentlandite–magnetite ± very minor awaruite. Some magnetite seems to have been added to the sulfide assemblages rather than to have replaced them.

3) During progressive serpentinization there was significant introduction of S from an external source which combined with Fe released by serpentinization of olivine to produce additional Fe sulfides or to replace magnetite and pentlandite at sites of pre-existing magmatic sulfides and to produce valleriite around composite magnetite–chromite grains (or both effects). Similar evidence for S introduction exists at Black Swan (Keays *et al.* 1979); Moeskops & Davis (1977) present textural evidence for such a process in the Bulong complex near Kalgoorlie.

4) There is some evidence for minor Ni loss from the silicate fraction during serpentinization.

5) Sulfides were recrystallized during progressive carbonation and, in at least some cases, the sulfide fraction appears to have lost Ni. There was no further addition of S, but S was possibly lost in some cases. Minor arsenic was introduced *via* the carbonate-bearing alteration fluids.

6) There was no systematic redistribution of Au at Mt. Keith–Betheno. The contrast in behavior of Au during alteration with that at Black Swan, where significant Au appears to have been lost during carbonation, may relate to the more oxidizing conditions of alteration at similar temperatures that existed at Black Swan.

7) The Ni tenor of the mineralization was only increased during incipient serpentinization. Original sulfide Ni was maintained or possibly even depleted during progressive alteration.

8) The increase in sulfide volume during alteration possibly represents an important initial stage in the formation of metamorphic massive ores in high-metamorphic-grade, high-strain environments.

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