Unusual sulphide replacement textures in altered olivine-rich rocks of the Bulong Complex near Kalgoorlie, Western Australia

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SUMMARY. Unusual replacement-type sulphide mineralization occurs in the northern part of the Bulong Complex, about 30 km east of Kalgoorlie, Western Australia. The mineralization is non-economic (up to 0·5 % Ni, 0·4 % Cu, 0·1 % Co, and 8·6 % S) and occurs in altered unlayered olivine-rich rocks immediately above a thin sheet-like inclusion of country rock. The supergene-modified primary opaque assemblage pyrrhotine-magnetite-pyrite-chalcopyrite-(pentlandite) is texturally unusual in that the opaques are largely pseudomorphic after primary olivine grains, mainly within irregular fracture networks in a manner similar to 'early' serpentine. Textural relations between opaques and silicates indicate that the mineralization was introduced during the early stages of serpentinization prior to the onset of deformation and regional metamorphism. Monoclinic pyrrhotine is the main opaque phase, with some grains containing relict cores of the hexagonal variety. Magnetite associated with the mineralization is Ni-poor ($< 0·1$ % Ni) compared with 'serpentinization magnetite' from elsewhere in the Bulong Complex, which contains 0·5-0·8 % Ni. As the mineralization was intersected at relatively shallow depth, supergene alteration effects are evident; pyrrhotine is locally altered to pyrite and marcasite (texturally and chemically distinct from the primary pyrite), and pentlandite is largely replaced by cupriferous violarite.

Textural features and consideration of phase relations in the system Cu-Fe-S-O suggest that the mineralization is of low-temperature ($350\pm$ °C) hydrothermal origin. By contrast, the more commonly developed Fe-Ni-Cu sulphide mineralization of the Kalgoorlie region is generally considered to be of high-temperature ($1200\pm$ °C) magmatic origin.

THE Bulong Complex was formally named by Williams (1969) and has been studied in considerable detail by Moeskops (1973). The Complex has a total strike length of some 37 km, centred near the deserted gold-mining camp of Bulong, about 30 km east of Kalgoorlie, where it occurs as four main limbs separated by an extensive saddle area (fig. 1). Throughout the Complex metaserpentinized olivine-rich rocks predominate, accompanied locally by minor amounts of pyroxenitic, gabbroic, dioritic, and granophyric rocks. Most ultramafic rocks of the Complex are altered layered cumulates, which have been deformed and tilted into steeply dipping attitudes. Detailed work on the Complex (Moeskops, 1973) has suggested that it originated as a series of ultrabasic and (fewer) basic magma pulses, which were injected into near-horizontal country rocks; larger pulses differentiated by convective-gravitational processes to produce layered sills, whereas smaller pulses simply froze to produce homogeneous sills or underwent flowage differentiation prior to freezing to produce symmetrically zoned sills. When igneous activity had virtually ceased, the Complex and its host rocks were regionally folded and metamorphosed.

The mineralization. The northern part of the Complex is locally mineralized (fig. 1). During 1968 six diamond drillholes were sunk into the mineralized area along a north-easterly section (fig. 2). Three of the holes encountered subeconomic sulphides (containing up to 0·5 % Ni, 0·4 % Cu, 0·1 % Co, and 8·6 % S) in altered homogeneous ultrabasic rocks immediately about a thin
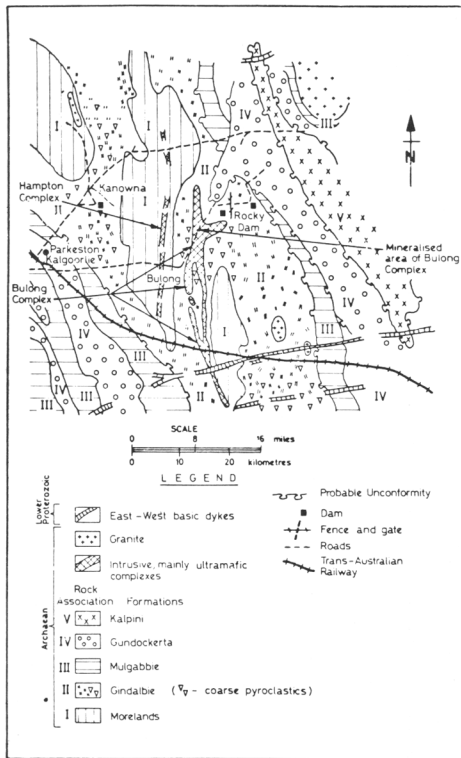
FIG. 1. Bulong Complex geological setting (after
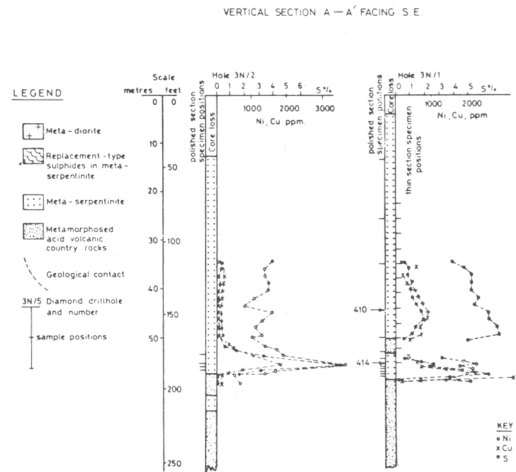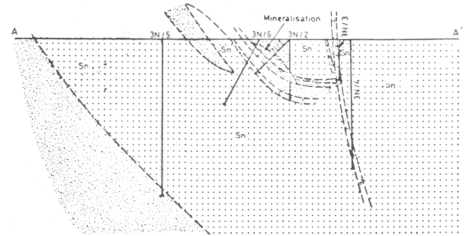Williams, 1969, modified by Moeskops, 1973).

FIG. 2. Bulong Complex: mineralized area of
north-west limb.

prow-shaped country rock sheet, as illustrated in fig. 2. Marked concentration of sulphides
towards the country rock sheet is reflected by increasing Cu, Ni, and S values in drill-cores (see
fig. 2). Examination of thin and polished sections indicated that the mineralization consists
of the supergene-modified primary opaque assemblage pyrrhotine-magnetite-pyrite-
chalcopyrite-(pentlandite). The texture is unusual in that the opaque assemblage has largely
pseudomorphed olivine grains, typically about irregular fracture networks in a manner similar
to early serpentine (fig. 3a–f). A small proportion of the opaques appears also to have partially
replaced interstitial clinopyroxene grains and in some sections chromite has also been partially
replaced. Introduction of the sulphide–oxide assemblage apparently coincided with early
serpentinization as primary serpentine cords and sulphide–oxide patches and veins mutually
cross-cut each other. Characteristically, however, opaques occur immediately about serpentine
cords partially replacing olivine relics between them. At a later stage during regional
metamorphism, recrystallization of serpentine and growth of fibrous tremolite and chlorite
caused extensive penetration of the opaques (especially pyrrhotine, along its main cleavage
direction). Whereas the over-all replacement texture is distinct in even the most intensely
metamorphosed samples, in microscopic detail the opaques contain numerous fine splinter- and
hair-like secondary silicate inclusions. Very fine alternating opaque-silicate lamellae, locally
bent into open microfolds or cut by microfaults, are also commonly seen.

   The mineralization was intersected at relatively shallow depth, hence the effects of supergene
alteration are locally marked. Pentlandite is almost entirely altered to cupriferous violarite of
unusual composition (Moeskops, 1975), and pyrrhotine exhibits incipient alteration to
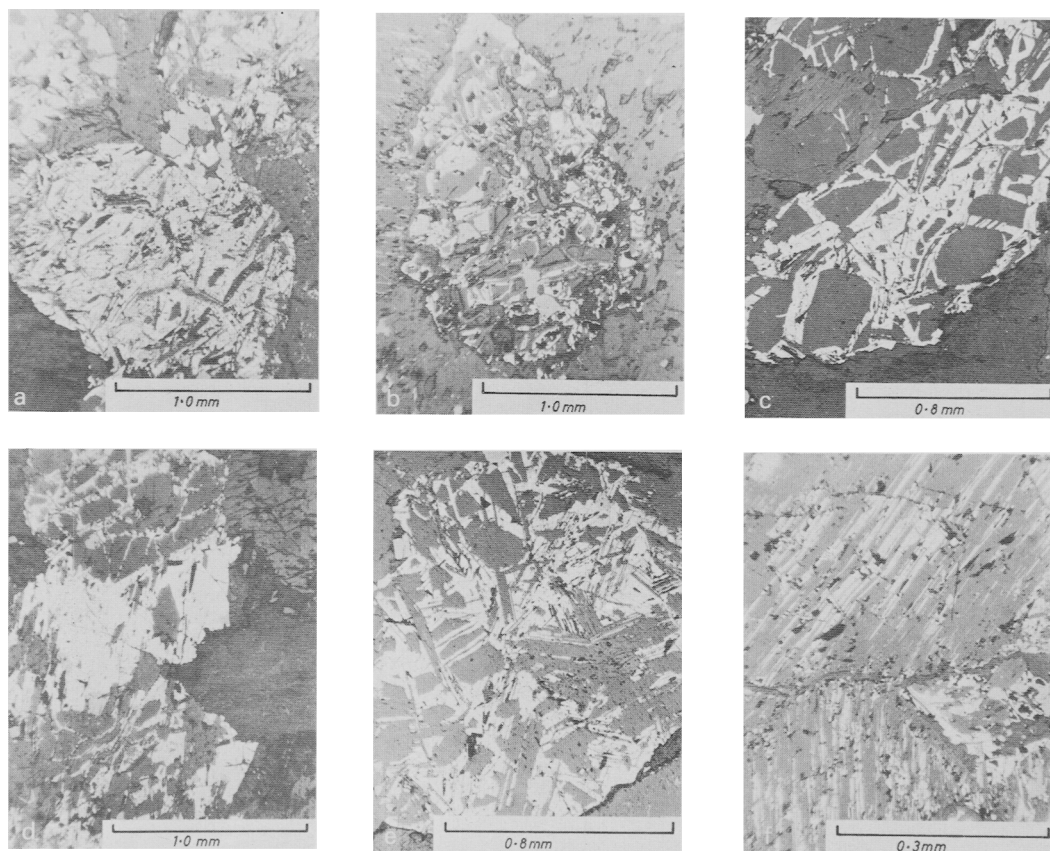
FIG. 3a–f. Photomicrographs showing olivine grains replaced (pseudomorphed) to varying degrees by the supergene-modified primary opaque assemblage pyrrhotine–magnetite–pyrite–chalcopyrite–(pentlandite). The texture is clearly different from that exhibited by magmatic Fe–Ni–Cu sulphides, which characteristically fill interstices between olivine grains. Fig. 3d shows an interstitial (? poikilitic) clinopyroxene grain, which has also been partially replaced by sulphides. During regional metamorphism olivine was largely altered to fibrous secondary silicates (mainly antigorite and tremolite), which have pierced and partially replaced the opaques (especially pyrrhotine) along cleavage directions (e.g. fig. 3e). This feature is well illustrated in fig. 3f, which shows two grains that have been largely replaced by fibrous antigorite. In all photomicrographs magnetite appears light to medium grey, silicates appear dark grey, and sulphides appear white to very light grey.

pyrite, which is locally associated with marcasite. Supergene pyrite retains the relict pyrrhotine cleavage pattern, which readily distinguishes it from primary pyrite. Within the oxidized zone above, chalcopyrite is replaced to varying degrees by microcrystalline chalcosine–covelline–goethite aggregates, and magnetite exhibits incipient martitization.

Some of the larger pyrrhotine grains were found by etching (with chromic acid) to contain small relict cores of hexagonal material surrounded by highly irregular interfingering rims of monoclinic material. Excluding a few primary igneous chromite grains (related to silicate crystallization and typically rimmed by secondary ferrochromite), all the pre-supergene opaque phases are very closely associated; contradictory cross-cutting and inclusion relationships are common and there is no evidence to suggest that any opaque phase was introduced into the rocks either before or after any other opaque phase. Exsolution phenomena are largely lacking though some magnetite grains contain a few thin exsolution lamellae of ilmenite. Since pentlandite (including its alteration product violarite) typically occurs about the boundaries of

pyrrhotine grains it seems likely that the pentlandite formed directly from pyrrhotine by grain-boundary exsolution processes.

Chemical and microprobe data. Mean pyrrhotine compositions, plus Co and Ni content of magnetite and pyrite, are listed in Table I. The data indicate that:

Compared with primary pyrite, supergene pyrite is enriched in Ni and depleted in Co. Compared with 'serpentinization magnetite' (from elsewhere in the Complex), magnetite associated with the mineralization is essentially devoid of Ni. And the hexagonal and monoclinic pyrrhotines possess compositions that lie close to those suggested by Arnold (1966). Violarite compositions and cell parameters are the subject of a separate publication. They are unusual (cupriferous) and lie within the composition range $Ni_{1.30-1.58}Fe_{1.57-1.19}Co_{0.21-0.13}Cu_{0.16-0.14}S_4$ (Moeskops, 1975).

TABLE I. *Pyrrhotine compositions and Ni and Co contents of pyrite and magnetite, determined by electron-probe analysis*

Pyrrhotine analyses (Wt%)			Ni and Co contents of magnetite and pyrite (Wt%)		
	Hexagonal cores	Monoclinic rims		Ni	Co
Fe	62·7	59·8	Magnetite of mineralized zone	< 0·1	< 0·1
Co	0·4	0·4	Serpentinization magnetite from throughout Complex	0·5–0·8	< 0·1
Ni	0·9	0·9	Primary pyrite of mineralized zone	0·3–0·5	0·5–0·9
S	36·5	39·4	Supergene pyrite (after pyrrhotine) of mineralized zone	0·8–1·1	0·3–0·7
Total	100·5	100·5			
Cations per 1 S					
Fe	0·982 ⎫	0·867 ⎫			
Co	0·006 ⎬ 1·00	0·006 ⎬ 0·89			
Ni	0·013 ⎭	0·012 ⎭			
S	1·00	1·00			
At% Fe	49·1	46·9			

Pyrrhotine analyses represent average of several 'spot' analyses on 4 to 5 grains in 3 polished sections. Magnetite and pyrite Ni and Co contents based on several spot analyses of 5 to 6 grains in 25 samples.

The opaque fraction of one relatively fresh, strongly mineralized drill-core sample (10 cm long) was separated, assayed for Cu, Ni, Fe, Co, and S and the normative mineralogy was calculated using compositions determined earlier by electron-probe analysis. Analytical data, weight norm data, and weight mode data (the last based on point-counting) are listed in Table II.

Discussion and conclusions. Replacement of primary and/or secondary mafic silicate minerals by Fe–Ni–Cu sulphides has been documented by a number of authors (e.g. Philpotts (1961), Chamberlain (1966), Naldrett (1966), Haapala (1969), and Genkin (1971)). Philpotts noted (in metaserpentinites of the Ungava area, Canada) the assemblage pyrrhotine-pentlandite-chalcopyrite replacing primary olivine and pyroxene relics, but not the associated secondary minerals such as amphibole, serpentine, and chlorite. Preferred replacement of anhydrous silicate relics in the presence of secondary hydrous silicates has also been recorded by Haapala (1969) in certain Fennoscandian Fe–Ni–Cu sulphide deposits, and Chamberlain (1966) has noted replacement of primary silicates by Fe–Cu sulphides near the roof of the Muskox Instrusion, Canada. Genkin (1971) has described veinlets of pyrrhotine and mackinawite 'outlining serpentine pseudomorphs after olivine' in basic-ultramafic masses near Norilsk,

TABLE II. *Weight mode and norm data for opaque fraction of strongly mineralized drill-core sample*

Element	Analysis of opaque fraction	Wt % of element (assumed SG's indicated in parenthesis)				
		Violarite (4·7)	Chalcopyrite (4·2)	Pyrite (5·0)	Pyrrhotine (4·6)	Magnetite (5·2)
Ni	1·23	0·38	0·00	0·00	0·85	0·00
Cu	0·76	0·04	0·72	0·00	0·00	0·00
Co	0·21	0·04	0·00	0·00	0·17	0·00
Fe	58·49	0·38	0·64	1·27	49·98	6·22
S	36·64	0·59	0·64	1·48	33·93	0·00
O*	2·67	0·00	0·00	0·00	0·00	2·67
				Calculated weight norm		
Wt % = 100·00		1·43	2·00	2·75	84·93	8·89

Weight mode

	Wt % for above assumed SG's	
Violarite	1·4	
Chalcopyrite	2·1	23·6 wt %
Pyrite	3·2	of total rock
Pyrrhotine	83·2	
Magnetite	10·1	

Norm calculated using over-all analysis of opaque separate, probe-determined composition of phases, and assumed SG's. Oxygen O* by difference; Cr_2O_3 ignored.

Mode calculated using point counting and assumed SG data. Silicate fraction (SG = 2·85) = 76·4 wt % of rock.

U.S.S.R., and also noted a 'very close relationship between serpentinisation and introduction of certain hydrothermal Fe–Cu–Ni sulphides'.

The literature indicates clearly that the assemblage pyrrhotine-pyrite-chalcopyrite-magnetite is common in certain hydrothermal deposits. The system Cu–Fe–S–O has only recently been studied (Taylor and Kullerud, 1970) and phase relations at 300 °C (fig. 4) are particularly important. The composition tetrahedron outlined by tie lines between the four phases mentioned above has a broad base, hence considerable variation in initial bulk composition does not change the assemblage. All phases coexist with vapour, and addition of Ni as a fifth component produces pentlandite as an additional phase at about 200 °C. The laboratory data were obtained by heating and quenching mixtures of pure Fe, Cu, and S with the oxides Fe_2O_3 and Fe_3O_4 and all tie-lines are between binary and ternary phases. The bulk composition of the separated opaque fraction (Table II), converted to atomic percentages in terms of the four components (ignoring Ni and Co) falls, as would be expected, within the composition tetrahedron formed by the four phases mentioned. Hence the assemblage probably formed under equilibrium conditions at constant oxygen fugacity—buffered presumably by the surrounding rock components (see Taylor and Kullerud, 1970). The presence of remnant hexagonal pyrrhotine in the assemblage implies a formation temperature in excess of 308–310 °C because below that temperature-range monoclinic pyrrhotine is the stable phase (see Kullerud et al., 1963; Desborough and Carpenter, 1965; Clark, 1966). The maximum temperature at which serpentinization can occur is generally thought to be about 500 °C (e.g. Turner and Verhoogen, 1960) and since the mineralization was clearly introduced during (early) serpentinization, the introduction temperature presumably lay between 308 and 500 °C. A reasonable guess would be about 350 °C because serpentinization generally occurs well below 500 °C (Martin and Fyfe, 1970). After introduction and partial replacement of primary silicates, the observed (i.e. pentlandite-bearing) assemblage would have formed, presumably by equilibrium cooling to about 200 °C.

The source of the mineralization was probably a late hydrothermal emanation representing the final fractionation product of an ultrabasic magma pulse. Such a fluid would probably be enriched in H_2O, S, Fe, and Cu and would contain little or no Ni because of the abundant entry of that element into early olivine (e.g. Wager and Vincent, 1957). Within the various layered (i.e. fractionated) ultrabasic series of the Bulong Complex there is a steady increase in the Co:Ni ratio in rocks and in minerals with increasing stratigraphic height (Moeskops, 1973), indicating that Co may have concentrated preferentially in residual fluids. Geochemical exploration of the Complex during the nickel boom led to the discovery of several Cu–Co anomalies in country rocks and late-stage basic to intermediate intrusive masses about the tops of layered ultramafic sills. These anomalies were normally found to be due to Cu-stained magnetite-bearing fractures,
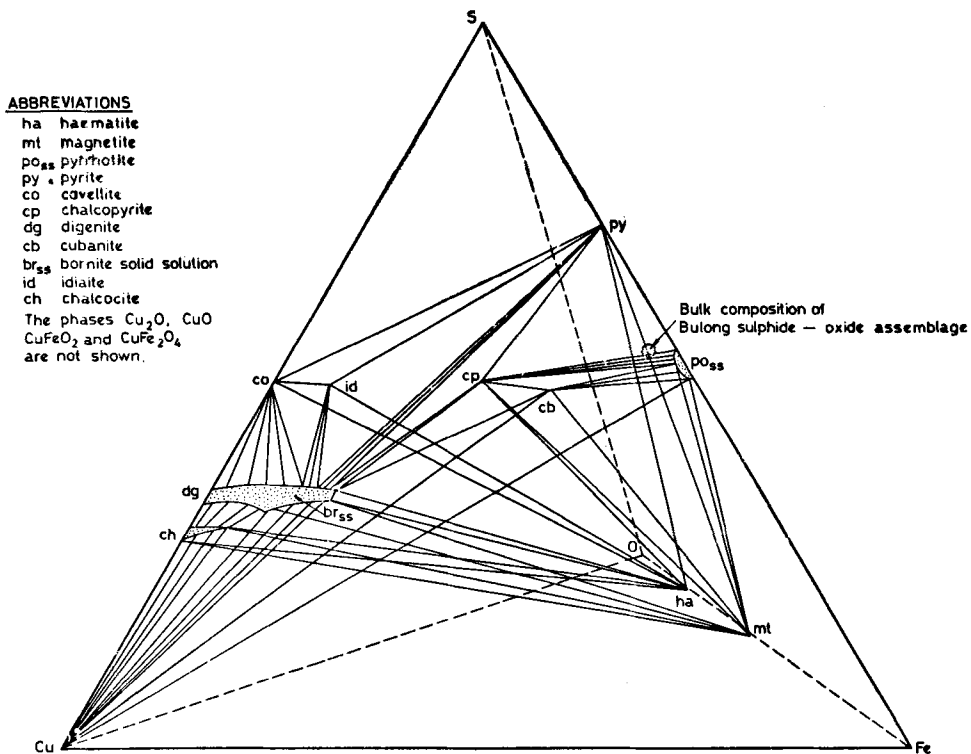

ABBREVIATIONS
ha   haematite
mt   magnetite
po$_{ss}$ pyrrhotite
py   pyrite
co   covellite
cp   chalcopyrite
dg   digenite
cb   cubanite
br$_{ss}$ bornite solid solution
id   idaite
ch   chalcocite
The phases Cu_2O, CuO
$CuFeO_2$ and $CuFe_2O_4$
are not shown.

Bulk composition of
Bulong sulphide – oxide assemblage

FIG. 4. Phase relations in the system Cu–Fe–S–O, 1 bar (after Taylor and Kullerud, 1970).

which suggests that small amounts of residual fluids enriched in Cu, Co, Fe, and S were produced as the final product of ultrabasic magma fractionation. Ni associated with the mineralization was probably extracted directly from the host rock silicates (mainly olivine) by the introduced hydrothermal fluids. This can be deduced from the fact that magnetite associated with the mineralization contains no detectable Ni whereas serpentinization magnetite in unmineralized rocks from elsewhere in the Complex contains 0·5–0·8 % Ni (see Table I). It is perhaps interesting to note that Fitzhugh and Seidel (1966) extracted Ni-rich sulphides from an aqueous slurry of native sulphur plus Ni-bearing silicates and oxides, at temperatures as low as 175–200 °C.

Progressive penetration and replacement of primary sulphides and oxides by secondary hydrous silicates during serpentinization and regional metamorphism has been noted by several

authors. For example Kilburn *et al.* (1969) have recognized five stages of alteration, and progressive penetration-replacement textures illustrated by those authors are virtually identical to those seen in the Bulong Complex, and for that matter, elsewhere in the Kalgoorlie region.

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