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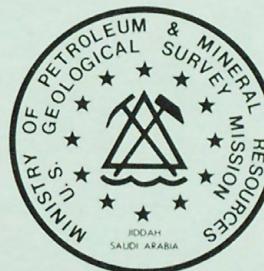
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MINERALIZATION AND GOSSANS IN THE WADI WASSAT-WADI QATAN REGION, KINGDOM OF SAUDI ARABIA
With a section on
# HYDROTHERMAL NICKELIAN MACKINAWITE AND ALABANDITE AT WADI QATAN

By

Christopher F. Blain
U. S. Geological Survey
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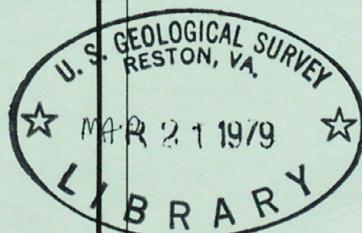
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CONTENTS

ILLUSTRATIONS

ii

MINERALIZATION AND GOSSANS IN THE

WADI WASSAT-WADI QATAN REGION, KINGDOM OF SAUDI ARABIA

by

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ABSTRACT

Very large bodies of stratabound iron sulfides in volcanic rocks of the Wadi Wassat-Wadi Qatan region of Saudi Arabia are capped at surface by numerous iron oxide-rich gossan outcrops. The gossan at Hadbah overlies a low-grade nickel-bearing sulfide body, but most of the sulfide lenses are almost devoid of base metals. Supergene alteration of pyrrhotite-pentlandite has given rise, in profile, to a narrow (<5 m thick) zone of violarite-pyrite (or marcasite) beneath an oxide zone (<35 m deep) of goethite-hematite-silica. Geochemical data show that, despite intensive leaching in the upper parts of the profile, the gossans over the nickeliferous sulfides have higher contents of trace metals than do the gossans overlying pyritic bodies. Both hypogene and supergene textures are well preserved in the gossans; in particular, the presence of very fine-grained pentlandite in the primary sulfide assemblage is precisely recorded by diagnostic replica textures in the gossans.

INTRODUCTION

The field relations of orebodies within geomorphologically mature terrains clearly show that most hypogene sulfide assemblages are unstable in the near-surface weathering regime,

1

particularly in the presence of oxidizing agents such as water-dissolved oxygen. The action of the oxidizing agents causes massive sulfide bodies to re-equilibrate electro-chemically and give rise to vertically zoned weathered profiles. Generally, the profiles consist of a hypogene sulfide zone at depth, which grades upwards through a more oxidized supergene sulfide zone into a leached oxide zone that is capped by goethitic, silica-rich gossans at the sur-face. Consideration of this total evolutionary sequence within the profile is extremely relevant to the interpretation of gossans because certain mineralogical, geochemical, and tex-tural features that are characteristic of the hypogene or supergene sulfides at depth may be only subtly preserved in the surface gossans.

Recent studies of the weathering of Kambalda-type nickel sulfide orebodies within semi-arid climatic terrains (Nickel and others, 1974; Brotherton, in prep.; Thornber, 1975a, b) have shown that massive pyrrhotite-pentlandite ores generally grade transitionally upwards in profile through stable assem-blages of violarite-pyrite (marcasite)-siderite into oxide zones of geothite-silica. Commonly, the oxide rocks and gossans inherit much of the textural fabric of the former sulfide assemblages (Nickel, 1973; Blain and Andrew, 1977) and, in addition, retain a significant component of the original sulfide-metal content (Wilmshurst, 1975; Blain and Andrew, 1977). The correct identification of nickel gossans within a background of other ironstones can therefore be achieved by

routine reference to trace element criteria based upon copper, nickel, cobalt, and chromium contents (Bull and Mazzucchelli, 1975; Joyce and Clema, 1974; Clema and Stevens-Hoare, 1973). In certain cases, even an estimated grade of the parent ore can be predicted from the contents of the immobile elements, palladium and iridium, in the gossan (Travis and others, 1976). Similarly, a nickel sulfide grade may be predicted by interpretation of replica textures in the gossan (Nickel, 1973; Roberts and Travis, 1973; Blain and Andrew, 1977). These specific geochemical and textural criteria are, of course, applicable only to that specific type of deposit within its own geomorphological and climatic setting. For other types of deposits elsewhere, the problem of assessing gossans may be manifestly different.

This work is concerned with the assessment of iron sulfide gossans and base-metal sulfide gossans within the climatically arid regions of Saudi Arabia. The Wadi Wassat-Wadi Qatan region in the southern part of the Arabian Shield is ideally suited to this type of assessment because of the large areal exposure of gossan overlying a mixed, though predominantly barren, sulfide facies. Previous work (Jackaman, 1972; Dodge and Rossman, 1975) has established that these large, areally continuous gossan zones mainly overly a monotonously pyritic or pyrrhotitic sulfide facies although at least one portion, the Hadbah gossan, overlies an anomalously nickel-rich, pentlandite-bearing sulfide zone. Regional evaluation of the sulfide facies, therefore, poses the problem of how the Hadbah

3

gossans can best be distinguished from gossans overlying 'barren' iron sulfide facies before it can be established whether the whole of this very large sulfide formation is entirely devoid of nickel or other base metals. This short report presents the results of preliminary geological work on the nickel-bearing sulfide assemblages at Hadbah and their overlying supergene-altered sulfide zones and gossans. The geochemistry of the gossans is dealt with in a subsequent report.

Imperial College, London.   Work in Saudi Arabia was performed
in accordance with a work agreement between the Saudi Arabian
Ministry of Petroleum and Mineral Resources and the U.S.
Geological Survey.

FIELD RELATIONS

Based upon descriptions and mapping of previous workers
(Jackaman, 1972; Dodge and Rossman, 1975; Overstreet and
Rossman, 1970; Greenwood,   1979;), syntheses of the geology of
the Wadi Wassat and Wadi Qatan regions are illustrated in
figures 1 and 2.   The oldest rocks in the region are Precambrian
metamorphosed volcanic extrusives (basalts) and volcanoclastic
sediments (andesitic tuffs, agglomerates, dacites, and rhyolite),
with interbedded exhalites and chemical sedimentary layers.
The stratabound sulfide mineralization of the Wassat and Qatan
formations is generally considered to be one or more of these
exhalite facies.   This supracrustal calc-alkaline volcanic
suite has been regionally metamorphosed and deformed and is
intruded by large dioritic and granitic plutons.   The entire
assemblage is transected by swarms of anastomosing dikes and
veins.

Under the prevailing geomorphological conditions, these
rocks are exposed as hilly areas of moderate (100-200 m) relief,
separated by alluvium-covered wadis.   The exposed rocks are
not, in general, intensively weathered although they are
commonly coated with a polished iron-rich film, the so-called
'desert varnish'.   The sulfide-bearing rocks, however, are
significantly weathered and outcrop as a variety of leached

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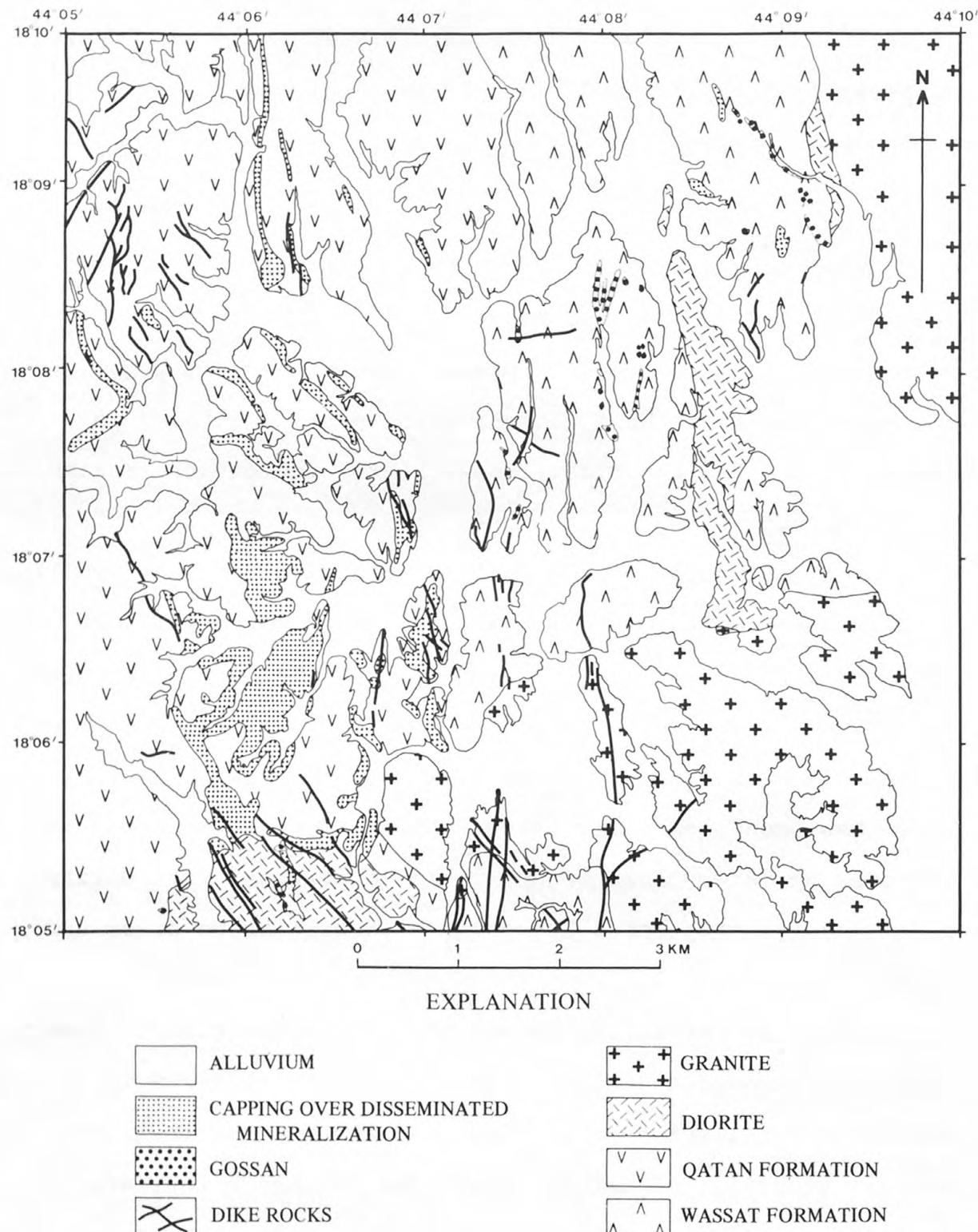
Figure 1. Geologic map of the Wadi Qatan area (adapted from Jackaman, 1972, Dodge and Rossman, 1975; Overstreet and Rossman, 1970, and Greenwood (1979). Note that the low-grade nickel mineralization of the Hadbah zone is expressed by the NNW — trending gossan outcrops at 18°09'N., 44°-09'E.

EXPLANATION

ALLUVIUM

CAPPING OVER DISSEMINATED MINERALIZATION

GOSSAN

DIKE ROCKS

GRANITE

DIORITE

QATAN FORMATION

WASSAT FORMATION

6

cappings and gossans (figs. 1 and 2). Data from drilling indicate that the sulfide-oxide weathering interface is generally about 10 to 40 m beneath the present land surface, at which depth it is evident that gossans are currently forming.

The gossans over massive sulfides are mainly composed of hematite and goethite, with varying amounts of jasperoidal silica. Some of the gossans are porous and have large macroscopically visible boxworks; others are almost massive. They range in color from rusty brown to steely black. Over matrix and disseminated sulfides, the cappings invariably contain remnants of the host silicate rock. Bedding in large remanent blocks included within the gossan zones is generally conformable with bedding in the adjacent rocks. The iron- and silica-rich gossans are stable and refractory, and commonly, though not ubiquitously, crop out as ridges and spines of hills. Collectively, these outcrops are exposed along 50 or 60 km of strike length, and, in places, are up to 100 m wide (figs. 1 and 2). On steep hill slopes, screes of mechanically transported gossan fragments are recemented as breccias, forming a discrete class of the so-called 'transported gossans' (Blain and Andrew, 1977). Examination of drill core shows that other types of gossan breccias occur below surface, presumably where they have formed by collapse of corroding sulfide blocks followed by recementation by iron oxides and silica. A variety of efflorescences occur on the bottommost slopes, both proximally and distally about the gossans. The common yellow-brown

EXPLANATION

Alluvium

Granite

Diorite

Andesite and andesite tuff

Sedimentary, pyroclastic, and
volcanic rocks; gossan at top

Contact

Fault

0   1   2 KILOMETERS

44°14'
18°23'

N

Geology by D. Rossman, 1967,
and R. J. Roberts, 1975
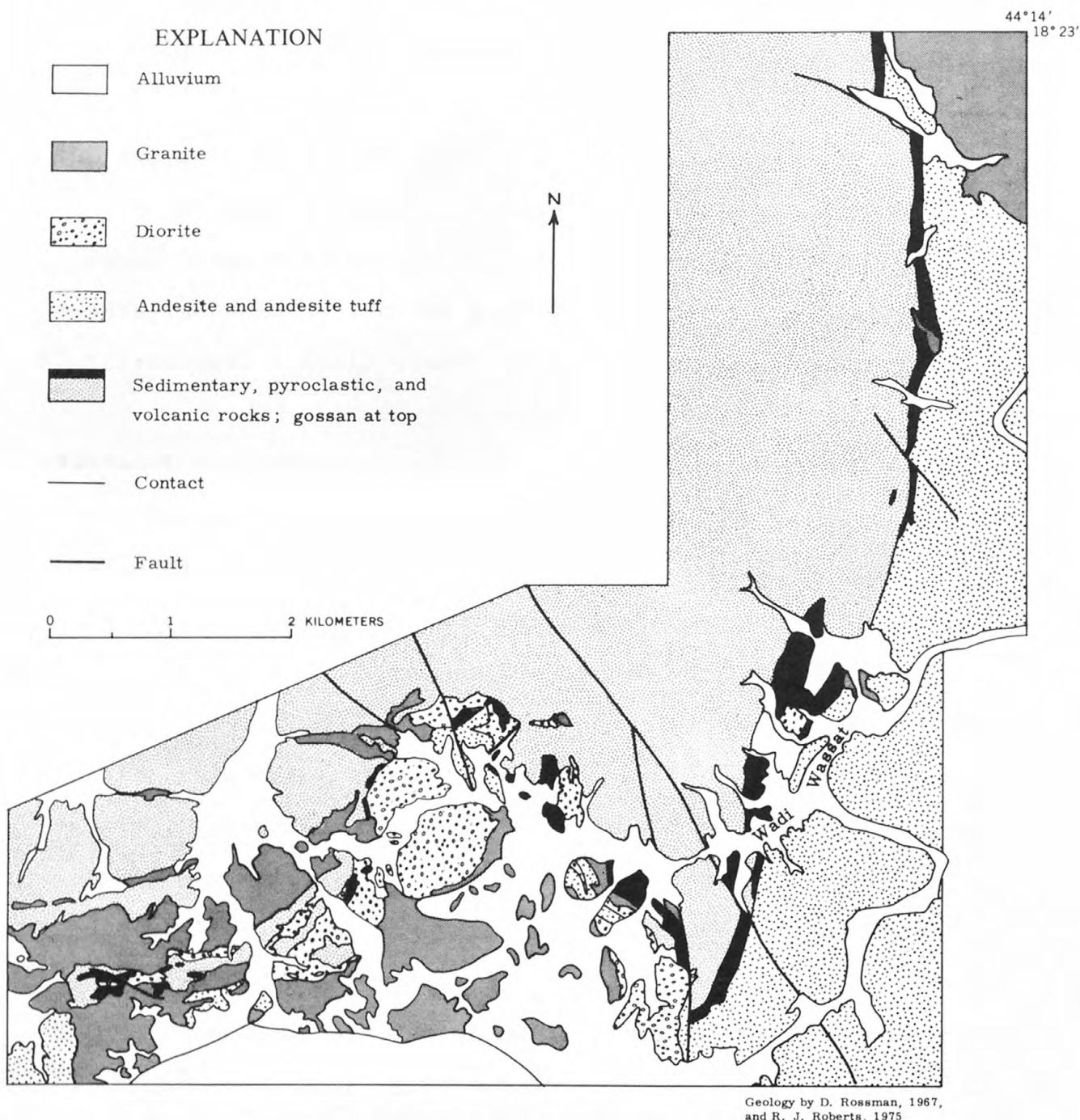
Figure 2. Generalized geologic map of the Wadi Wassat area (from Roberts, 1976, p. 21).

form has been established by X-ray diffraction to be mainly jarosite, $KFe_3(SO_4)_2(OH)_6$, and superimposed white crusts are rich in bloedite, $Na_2Mg(SO_4)_2 \cdot 4H_2O$. These efflorescences are considered to originate by the oxidation of sulfides, and thus testify to active gossan formation at the present time.

PRIMARY SULFIDE MINERALIZATION

The spectacular gossans at Wadi Wassat and Wadi Qatan were first noted in modern times during the course of regional mapping in 1952 (Brown and Jackson, 1959), but their exploration significance became more fully appreciated during the reconnaissance work of a private prospector, Hatim Khalidi, in 1964 (H. Khalidi, pers. commun.). Subsequent mapping and drilling (Overstreet and Rossman, 1970) revealed the presence of numerous massive and richly disseminated pyritic lenses lying conformably within basaltic and andesitic rocks. Individual lenses are steeply dipping and stratigraphically continuous for distances up to 4 or 5 kms, and have true thicknesses ranging up to 85 or 100 m. The lenses are folded and faulted (figs. 1 and 2). In places, the volcanics and contained sulfide lenses are truncated by large bodies of intrusive diorite, around which the rocks are thermally metamorphosed. One or two of the lenses in the Wadi Wassat area persist within the outer margin of the diorite as disconnected septa of pyrrhotite-mineralized rock. The field relations strongly suggest that the pyrrhotite mineralization represents contact-metamorphosed pyrite (Jackaman, 1972).

9

The mineralogy and textures of the sulfide lenses in the Wadi Wassat and Wadi Qatan regions have been described in considerable detail by Jackaman (1972). The paragenesis consists mainly of pyrite and pyrrhotite with trace amounts of sphalerite and chalcopyrite. Commonly, the massive and disseminated pyritic layers show well preserved laminated bedding although the pyrite also occurs as several generations of crosscutting veinlets. Small zones of pyrite are cataclastically deformed. Despite the preservation of the original lamination, there seems to be little doubt of a predominantly recrystallized, or at least overgrown, fabric. The recrystallized fabric may well reflect the response of the sulfide lenses to superimposed regional deformation and greenschist-facies metamorphism.

Subsequent exploration in 1972 in the Wadi Qatan region by the Arabian Shield Development Company led to the discovery of low-grade nickel mineralization a few kilometers east of the areas previously examined (Dodge and Rossman, 1975). This sulfide mineralization in the Hadbah zone (fig. 2, 18°09'N., 44°09'E.) occurs over a thickness of up to 30 m within an assemblage of basalts, andesitic tuffs, and agglomerates (Dodge and Rossman, 1975) adjacent to intrusive diorite.

The nickel mineralization consists of pyritic, pyrrhotitic, and mixed pyritic-pyrrhotitic facies, all of which contain minor amounts of pentlandite. Assay data indicate that the nickel:sulfur ratio (by weight) rarely exceeds about 1:8 or 1:10 in samples of hand specimen size. Electron probe micro-

analysis shows that pentlandite, of composition $Fe_{4.8}Ni_{4.2}S_8$ (based on 50 point analyses), is the main nickel-bearing phase although lesser concentrations of nickel, ranging from 0.3 to 1.4 percent and averaging 0.7 percent by weight (based on 20 point analyses), occur within pyrite. Nickel:cobalt ratios of approximately 5:1 for pyrite appear to be much higher than those for pyrite in nickel ores in mafic-ultramafic association (Nickel and others, 1974; Fleischer, 1955; Hawley, 1962). Another unusual feature of the Hadbah mineralization is its assemblage of sulfide minerals. As well as chalco-pyrite, the assemblage contains minor amounts of sphalerite, cubanite, molybdenite, and alabandite. Some of the pentlandite and alabandite has altered to nickelian mackinawite, presumably under low-temperature hydrothermal conditions (see following Section).

The pentlandite-bearing pyrrhotite facies has a marked granoblastic fabric composed of anhedral and subhedral grains (av diam 100-400 μm) set within a silicate matrix (fig. 3 e, g). In this sulfide type, the pentlandite occurs as fine (5-40 μm long) flame-shaped inclusions in pyrrhotite, radiating from grain margins and twin boundaries. The orientation of these pentlandite flames is crystallographically controlled by the pyrrhotite host (fig. 3 e, g) and reflects an unmixing texture caused by subsolidus cooling of the parent monosulfide solid solution. Coarser (50-100 μm av diam) discrete grains of pentlandite (fig. 3 g) are isotropically distributed.

11
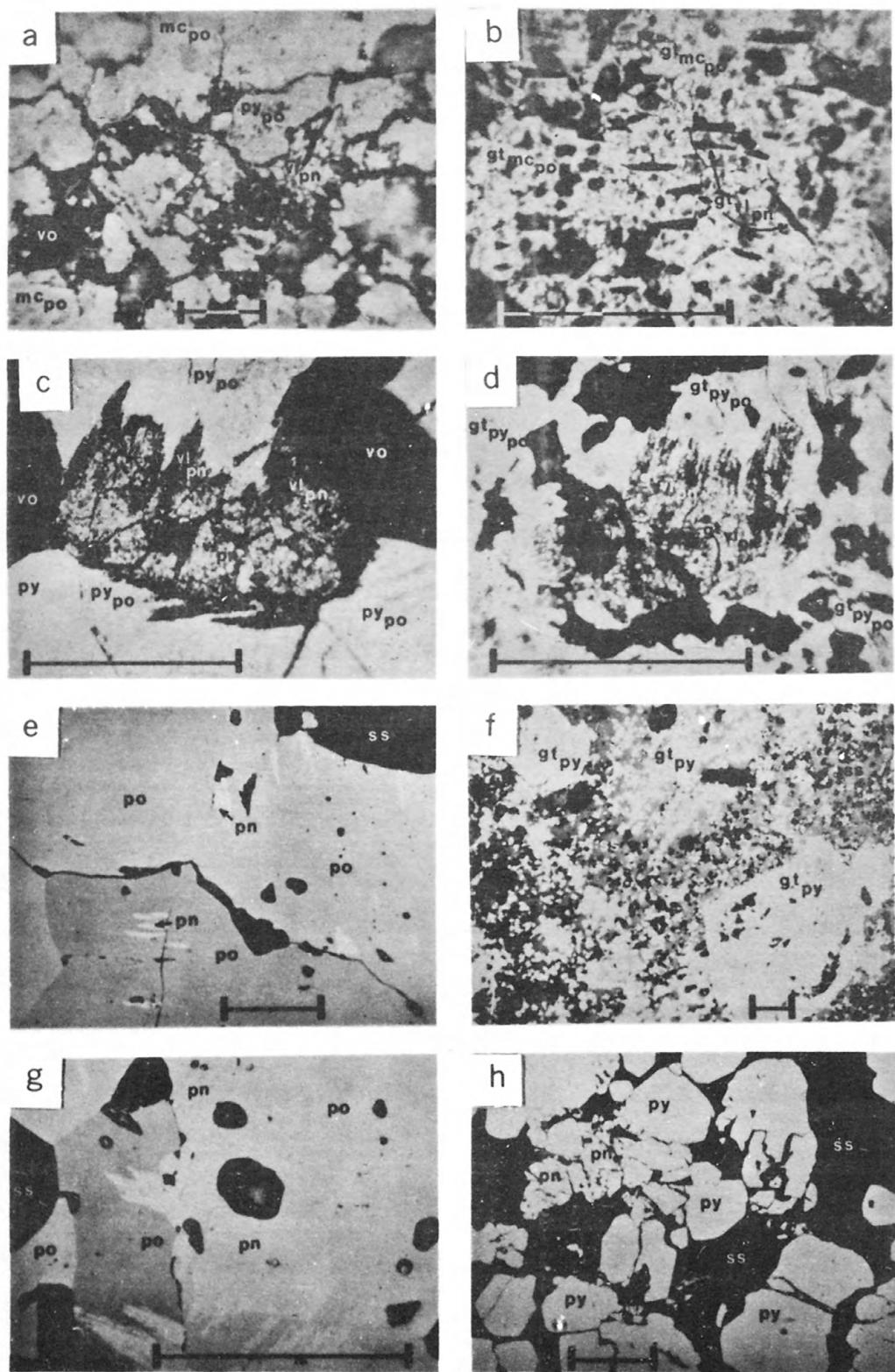
Figure 3. Caption on following page.

Figure 3. Photomicrographs illustrating the principal mineralogical and textural relationships of the hypogene mineralization (e, g, h), its supergene sulfide alteration (a, c), and overlying gossans (b, d, f). All samples are from the Hadbah zone in the Wadi Qatan region (fig. l). Subscripts denote the replaced mineral.

At depth, pentlandite (pn) occurs as discrete grains (fig. 3g) and small crystallographically oriented flames (fig. 3e, g) within a matrix of pyrrhotite (po) and silicate minerals (ss). In this sulfide type, pyrrhotite has a distinct granoblastic texture (fig. 3e, g) of roughly equant grains with slightly curved mutual boundaries. In the pyritic type, pentlandite occurring only as discrete grains and pyrite subhedra and euhedra of approximately the same size are set within a silicate matrix (fig. 3h). During supergene alteration, pentlandite alters to violarite (vl), and pyrrhotite alters either to pyrite or marcasite (fig. 3a, c). Note that hypogene pyrite, in association with supergene pyrite, is not altered (fig. 3c) although supergene pyrite and marcasite after pyrrhotite contain voids (vo) suggestive of sulfide dissolution or volume reduction (fig. 3a, c). In small areas, the supergene pyrite replacement may be almost pseudomorphous (fig. 3a, c) or finely colloform (fig. 3c) whereas the supergene marcasite is finely granular (fig. 3a). In the gossans, many of the textural features of hypogene and supergene sulfide assemblages are extremely well preserved by goethite. Goethite (gt) replacement textures in the gossan of hypogene pyrite may be almost massive (fig. 3f) although the cores of the larger grains are generally porous. The structure of the goethite that replaces supergene pyrite (after pyrrhotite) (fig. 3d) or supergene marcasite (after pyrrhotite) (fig. 3b) is more irregular and appears to reflect preferential precipitation of goethite around grain boundaries. Diagnostic replica textures of finely porous goethite after violaritized pentlandite are common in the gossans (fig. 3b, d). Both textural types of pentlandite, discrete grains (fig. 3d; cf. fig. 3c, g) and flames (fig. 3b; cf. fig. 3e), are in some gossans pseudomorphed accurately to the limits of optical resolution.

Length of all scale bars is 50 μm. All photomicrographs except figure 3f were taken under oil immersion. Figures 3b, c, d, f, and h were taken under plane-polarized reflected light whereas figures 3a e, and f were taken under partially cross-polarized reflected light.

In the mixed pyrite-pyrrhotite facies, the pyrite has a similarly anhedral aspect, texturally identical to the pyrrhotite. Unambiguous textural evidence of microfaulting and pyrite veining indicates, at least locally, that pyrite pervasively replaces pyrrhotite. Where pyrrhotite remains, it contains the characteristic flame-textured pentlandite, but pentlandite in the pyritic portions ubiquitously forms discrete anhedra and subhedra of grain size approximately that of the adjacent pyrite. In the pyritic facies, the pyrite is distinctly subhedral (fig. 3 h). Where pyrite is coarser grained, in veinlets for example, the associated pentlandite is also coarser. In places, traces of pyrrhotite occur inter-stitially to the triple junctions of pyrite subhedra. All of these observations on the pentlandite-bearing pyritic rocks could perhaps suggest that these pyrites have grown porphyro-blastically within the pyrrhotite matrix and that the nickel has redistributed as discrete pentlandite grains.

The sulfide textures in the Hadbah mineralization are complex in detail, and a more complete interpretation of this sulfide type must await more detailed work. Field and textural evidence leave little doubt that primary pyrite has been altered to pyrrhotite in response to proximate intrusions of granite and diorite. The textural evidence indicates that some of the pyrrhotite so formed could have been subsequently re-pyritized, perhaps by expelled sulfur. It is quite possible that under the pressure, temperature, and sulfur-fugacity conditions prevailing during regional metamorphism and pluton

14

emplacement, the proximate zones of the pre-existing pyrite lens could have equilibrated compositionally as a pyrrhotitic monosulfide solid, at which time there was an addition of nickel from the surrounding host rocks. Alternatively, a large component of the nickel may have been contained in the pre-existing pyrite. In any event, much of the nickel is now contained in small flame-shaped inclusions of pentlandite in pyrrhotite-rich sulfides and discrete grains in the pyritic type. From the viewpoint of interpreting textures in the gossans, the occurrence of pentlandite distinguishes the nickel-enriched Hadbah mineralization from the known nickel-poor iron sulfide mineralization elsewhere in the region.

SUPERGENE-ALTERED PROFILE

Mature supergene alteration of pyrrhotite-pentlandite orebodies typically persists well below the contemporary water tables (Nickel and others, 1974; Brotherton, in prep.; Blain and Andrew, 1977). Generally, the pyrrhotite-pentlandite assemblage at depth is connected to well developed zones of violarite and pyrite (or marcasite)* by transitional zones* where over considerable vertical intervals pentlandite and some of the pyrrhotite are partially replaced by violarite. Above the water tables, the sulfides grade sharply into oxide zones* of goethite, hematite, and silica.

At Hadbah, the sulfide-oxide weathering interface is about 35 m below surface. Selected samples of drill core through

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*The terminology used in this paper is consistent with that used by Nickel and others (1974).

15

the supergene-altered profile have facilitated a preliminary examination of the mineralogical and chemical changes in the formation of gossans over the pentlandite-bearing pyrrhotitic rocks. Surprisingly, in view of the relatively deep oxide zone, supergene alteration in the sulfide zone is confined to a narrow (<5 m) vertical interval immediately beneath the oxides. Further, there is no transition zone. The deepest supergene alteration consists of very small (∿1 mm across) areas where both pyrrhotite and pentlandite are transformed to pyrite (or marcasite) and violarite together. Outside these areas no pentlandite is visibly violaritized. Thus, the pro-file consists of hypogene pyrrhotite-pentlandite overlain by a narrow violarite-pyrite zone, in turn overlain by a thick oxide zone.

The chemical reactions for the deepest supergene altera-tion at Hadbah can be expressed in the general form at constant sulfur as follows:

$$(Fe,Ni)_9S_8 \longrightarrow 2(Fe,Ni)_3S_4 + 3(Fe^{++},Ni^{++}) + 6\;\bar{e}$$

(violaritization of pentlandite)

$$2FeS \longrightarrow FeS_2 + Fe^{++} + 2\;\bar{e}$$
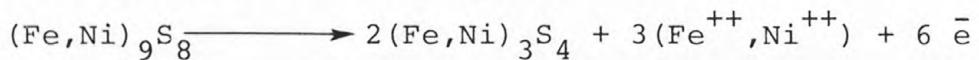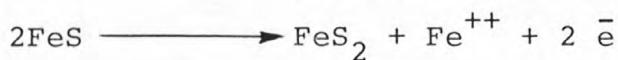
(pyritization of pyrrhotite)

Both of these reactions are oxidational (electron-producing) and demand the release of considerable amounts of iron and lesser amounts of nickel. In many supergene-altered profiles, the release of nickel is accounted for by the violaritization of surrounding pyrrhotite (Nickel and others, 1974), and the release of iron is accounted for by the precipitation of

16

supergene siderite (Nickel and others, 1974) or magnetite (Nickel and others, 1977). At Hadbah, where supergene violarite and pyrite form together, probe data indicate a slight enhancement in the nickel content of the pyrite, an enhancement which is certainly sufficient to account for nickel expelled by violaritization. However, no other supergene iron-bearing phase has been recognized in association with the supergene pyrite. It is suggested that the iron released under these conditions must be accounted for by entering the supergene liquid phase as a more mobile soluble form. It is perhaps significant that approximately 40 or 50 percent of the original pyrrhotite volume is estimated to be occupied by irregular 'dissolution' voids (fig. 3 a, c) in the contiguous supergene pyrite alteration. The supergene pyrite commonly shows the characteristic bird's-eye texture of spheroidal layers (fig. 3 c) indicating a systematic volume decrease. In places, supergene marcasite in granular form pseudomorphs pyrrhotite (fig. 3 a). Where the violarite-pyrite zone is well developed, there is an abundance of gypsum, recognizable in hand specimen. Presumably this sulfate has percolated down several meters from where the overlying sulfides are actively dissolving.

Above the sulfide-oxide interface, the violarite-pyrite assemblage is altered to hematite and goethite, and minor amounts of jasperoidal silica. The influx of silica is considered to testify to the intensity of hydrolysis-type weathering reactions in the surrounding silicate rocks that must

17

counteract and buffer the acid-producing sulfide-decomposition reactions. A surprising feature of the oxide rocks (and gossans) so formed is the almost perfect preservation of hypogene and supergene sulfide textures, discussed below.

The main chemical changes in the overall supergene alteration sequence are illustrated in figure 4 in which the weight equivalents per unit volume for iron, nickel, manganese, cobalt, and copper in samples of drill core are plotted against the distance from the surface along the drill hole. Weight equivalents per unit volume are used in order to eliminate apparent enrichment or depletion effects that may be related to differing specific gravity, porosity, or bulk composition. The equivalents thus portray only the relative spatial migration of elements into or out of the system. The figure shows a marked depletion in iron corresponding to pyritization of pyrrhotite. At this position, there is also considerable depletion in manganese, which is presumably caused by the dissolution of trace alabandite. Where the sulfides are transformed to oxides, all elements other than iron, but particularly nickel and cobalt, are thoroughly leached. A small component of the leached nickel may have re-entered the supergene sulfide system by reacting with and enriching the uppermost violarite. Probe data (average of 10 point analyses) show that the nickel content of the uppermost violarite (Ni:Ni + Fe = 0.65:1) is enhanced over that of the lowermost violarite (Ni:Ni + Fe = 0.50:1), corresponding with the thin zone of nickel enrichment (fig. 4). Even so, this enrichment

18

accounts only for a fraction of the nickel released by sulfide dissolution in the oxide zone. Almost all of the released nickel and for that matter all other metal cations with the exception of iron must have been flushed out of the gossan-forming system. Figure 4 indicates that most of the iron has precipitated *in situ* giving rise to ferruginous oxide rocks that crop out abundantly as gossans.

GOSSANS

Generally, the Hadbah gossans are massive in appearance although invariably they are finely porous on a small scale. No obviously diagnostic boxworks are visible in hand specimen because the hypogene and supergene sulfides are so fine-grained. Examination of polished surfaces by optical microscopy, however, reveals that the textural features of the former sulfides are well preserved in the gossans (fig. 3 b, d, f). On the scale of millimeters, the overall sulfide fabric is generally visible as a goethitic or hematitic replacement. In places, only the rims of the larger sulfide grains are outlined by goethite and the cores are represented as voids. Although pervasive flooding by introduced goethite and silica and thorough leaching have both obliterated the former sulfide fabric locally, the textures are well enough preserved to identify the precursory sulfides in almost all the samples examined.

Replicas of hypogene pyrite occur as near-perfect solid pseudomorphs in the subhedral and euhedral forms of cubes and pyritohedra as well as the disseminated interstitial matrix (fig. 3 f). Quite commonly only the outer rims of the larger
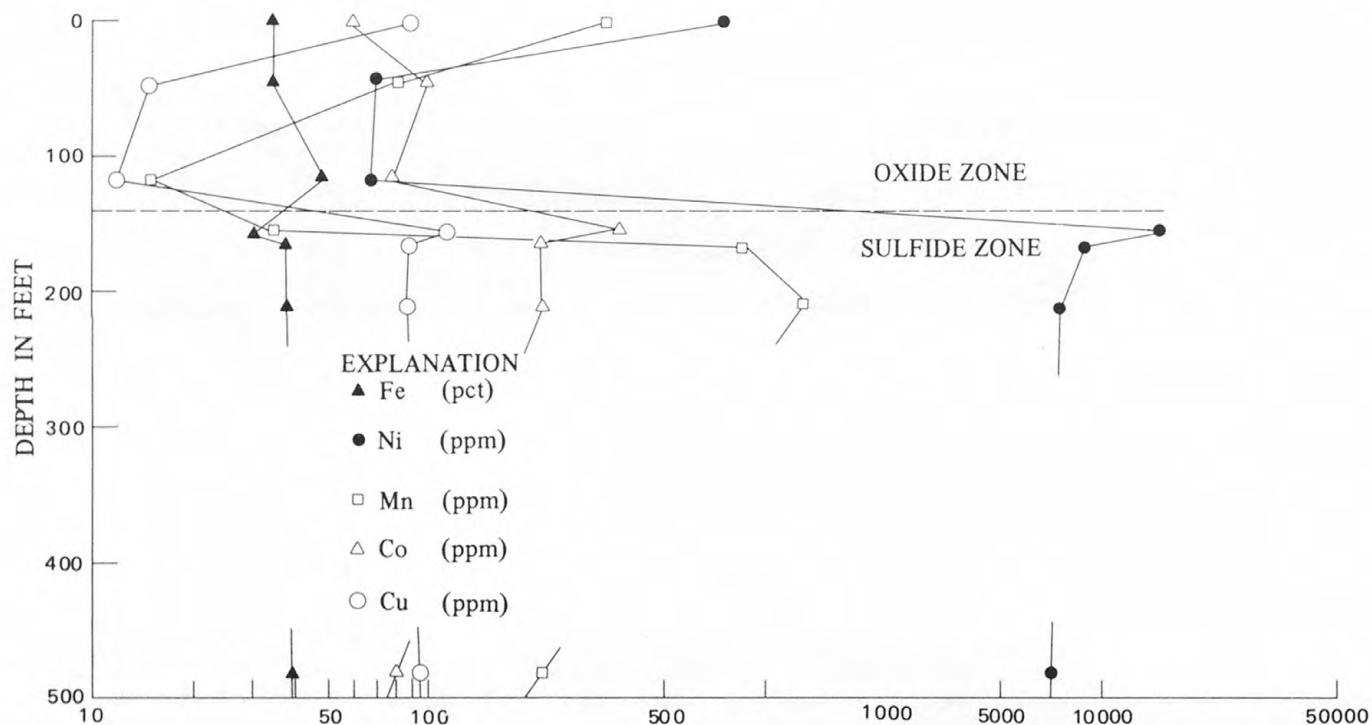
Figure 4. Geochemical variation trends in the supergene-altered pyrrhotite-pentlandite mineralization of the Hadbah zone, Wadi Qatan. Element contents, in weight equivalents per unit volume, are plotted on a logarithmic scale against distance from the surface in drill hole 3 (inclined hole). The contact between fresh rock (sulfide zone) and the zone of supergene alteration (oxide zone) is indicated on the diagram. The procedure of converting geochemical analyses of each element (by weight) into weight equivalents per unit volume (volume is assumed to be constant, and the conversion factor is the density of the solid and included pore space divided by atomic weight of a given element) eliminates the apparent enrichment or depletion effects related to differing specific gravity, porosity, and composition. The trends thus depict only the spatial migration of elements into or out of the profile. The assumption of constant volume appears reasonable because pre-existing sulfide textures are very commonly pseudomorphed in the gossans (fig. 3). Average bulk-density values used for conversion are 3.75 g/cc for pyrrhotite-pentlandite, 3.30 g/cc for violarite-pyrite, and 2.48 g/cc for oxides.

subhedra and euhedra are massively pseudomorphed and the internal structure is preserved as a delicate symmetrical boxwork. In places, even an internal zoning of pyrite is suggested by the goethitic replacement. Similarly, most of the supergene pyrite and marcasite (both after pyrrhotite) forms are evident in the gossans. The most common texture representing original pyrrhotite consists of poorly connected cell walls without an obviously systematic morphology (fig. 3 d); this is the so-called 'hieroglyphic' boxwork (Blain and Andrew, 1977), which presumably in this case largely reflects the position of former grain margins. Pseudomorphs of the less common bird's-eye texture (Blain and Andrew, 1977) of spheroidal supergene pyrite and marcasite (after pyrrhotite) layers are also present. The equidimensional granular form of supergene marcasite (after pyrrhotite) is portrayed in the gossan by the occurrence of numerous dissolution pits within goethite, each separated by several straight, but inconsistently oriented, cell walls (fig. 3 b). These probably reflect the positions of former marcasite grain margins (c.f. fig. 3 a). All of these textures are criteria for discriminating between gossans derived from the pyrrhotitic and those derived from the pyritic sulfide types.

The most significant feature of the textural work on the Hadbah gossans is the recognition of diagnostic replicas of pentlandite. This has been achieved by mineragraphic examination using high-resolution oil-immersion lenses at large magnifications. Figure 3 b, d show how perfectly these

21

textures are preserved in dark outline within pseudomorphed pyrrhotite. Violaritization of pentlandite in the violarite-pyrite zone at this locality takes place without forming additional violarite from pyrrhotite and, therefore, these replica textures probably indicate the volume occupied by original pentlandite only (cf. fig. 3 e, g). Both types of hypogene pentlandite are pseudomorphed, the flame textures (fig. 3 b, d) and the discrete grains (fig. 3 d). This preservation has probably been accomplished by the relatively rapid dissolution of violarite (after pentlandite), which is highly unstable in the presence of atmospheric oxygen above the contemporary water table. Rapid removal of nickel and sulfur probably leaves a cast containing a minor residue of goethite. The cast is evidently preserved as the surrounding supergene pyrite or marcasite (after pyrrhotite) alters *in situ* to more massive goethite. The orientation of the pentlandite flames in the original pyrrhotite is controlled crystallographically and, therefore, the preservation of flame textures in the gossan with two flame orientations (fig. 3 b) signifies the former presence of an intervening pyrrhotite grain boundary. There is no doubt that these textures, which may be relatively abundant in gossan samples containing as little as <100 ppm nickel, are wholly diagnostic of precursory pentlandite.

Geochemical analyses of a relatively small number of samples indicate that the gossans overlying low-grade nickel mineralization at Hadbah can be distinguished from those over

a drilled massive pyrite zone in the Wadi Wassat area by their

trace-element contents:

Nickel Gossan Zone, Hadbah (n = 15)

	Ni	Cu	Co	Mn	Zn
$\bar{x}$	220	55	55	250	45
r	25-1400	20-150	20-120	50-600	10-150

Pyrite Gossan Zone, Wassat (n = 15)

$\bar{x}$	30	20	20	150	20
r	10-90	5-50	10-30	50-260	5-35

where, n is the number of samples, $\bar{x}$ is the approximate geo-
metric mean (in ppm), and r represents the range (in ppm)
estimated at the 10 and 90 percentiles. The nickel content
is the best discriminator, but the higher contents of copper,
cobalt, manganese, and zinc in the Hadbah gossans are probably
good ancillary discriminators related to the trace occurrence
of chalcopyrite, cubanite, alabandite, and sphalerite in the
underlying sulfide assemblage. High molybdenum contents
relating to trace molybdenite in the sulfide mineralization
might similarly characterize these gossans. The ranges of
trace element variation in the gossans are largely independent
of their iron and silica contents, and the available geological
evidence suggests that gossan geochemistry correlates well
with the geochemistry of the underlying sulfide zones. Most
of the gossans in the region have been recently sampled in
detail by the U.S. Geological Survey, and preliminary geo-
chemical data reveal only subtle variation. Detailed work is
currently underway to quantify the multi-element geochemical
relationships between the drilled zones of sulfide mineralization

and their overlying gossans by applying multivariate statistical techniques. These techniques might then be applied to predict variations in the base-metal content of sulfide mineralization elsewhere in the region by variations in gossan geochemistry.

CONCLUSIONS

The problem of evaluating gossans overlying extensive zones of iron sulfide mineralization is highlighted in the Wadi Wassat-Wadi Qatan region of Saudi Arabia by the recent discovery of an associated pentlandite-bearing zone at Hadbah. Mineragraphic examination of the Hadbah mineralization reveals pyritic and pyrrhotitic rocks containing significant amounts of pentlandite and trace amounts of chalcopyrite, sphalerite, cubanite, alabandite, molybdenite, and nickelian mackinawite. This unusual assemblage of sulfide minerals is stratabound within metamorphosed volcanic rocks intruded by granite and diorite.

By supergene alteration, the pyrrhotite-pentlandite rocks have formed into a narrow violarite-pyrite layer and a thick (35 m) overlying blanket of goethite and hematite. Chemical data show that considerable leaching of all sulfide-bound metals, except iron, takes place where sulfide is oxidized to sulfate. Despite leaching, there is no doubt that the Hadbah gossans retain sufficient trace-element content to be distinguished from gossans over 'barren' iron sulfide mineralization. Further, the gossans contain almost perfectly preserved

microscopic textures indicating the presence of pentlandite in the original sulfide assemblage.

These data suggest that variations in the base metal content of the extensive sulfide mineralization in the region can potentially be predicted by recognition and interpretation of more subtle variations in gossan geochemistry. Probably, the best practical procedure for attaining this capability to predict is first to quantify empirically the relationships between sulfide and gossan geochemistry at drill sites by multivariate statistics. The predictor equations or discriminant functions so derived could then be used to evaluate routinely gathered geochemical data on gossans on a regional basis. The gossans from specific areas that appear to be of interest may then be evaluated by more time-consuming mineragraphic methods to interpret the nature of the sulfide assemblage. This approach is probably applicable to other regions where areally extensive zones of predominantly iron sulfide mineralization pose a similar exploration problem.

REFERENCES

Blain, C.F., and Andrew, R.L., 1977, Sulphide weathering and the evaluation of gossans in mineral exploration: Minerals Sci. Engng., v. 9, no. 3, p. 119-150.

Brotherton, R.L., in prep., The geology and geochemistry of nickel gossans within semi-arid climatic terrains: Ph.D. thesis, University of London.

Brown, G.F., and Jackson, R.O., 1959, Geologic map of the Asir quadrangle, Kingdom of Saudi Arabia: U.S. Geol. Survey Misc. Geol. Invest. Map I-217A, scale 1:500,000.

Bull, A.J., and Mazzucchelli, R.H., 1975, Application of discriminant analysis to the geochemical evaluation of gossans, in Elliott, I.L., and Fletcher, W.K., eds., Geochemical Exploration 1974: Elsevier, Amsterdam, p. 219-226.

Clema, J.M., and Stevens-Hoare, N.P., 1973, A method of distinguishing nickel gossans from other ironstones on the Yilgarn Shield, Western Australia: J. Geochem. Explor., v. 2, p. 393-402.

Dodge, F.C.W., and Rossman, D.L., 1975, Mineralization in the Wadi Qatan area, Kingdom of Saudi Arabia: U.S. Geol. Survey open-file rept. (IR)SA-190, 71 p.

Fleischer, M., 1955, Minor elements in some sulfide minerals: Econ. Geol. Fiftieth Anniversary Volume, part II, p. 970-1024.

Greenwood, W.R., 1979, Geology of the Wadi Wassat quadrangle, sheet 18/44C, Kingdom of Saudi Arabia: Saudi Arabian Dir. Gen. Mineral Resources Geol. Map GM-40, scale 1:100,000.

Hawley, J.E., 1962, The Sudbury ores: their mineralogy and origin: Can. Mineralogist, v. 7, part 1, p. 68.

Jackaman, B., 1972, Genetic and environmental factors controlling the formation of the massive sulphide deposits of Wadi Bidah and Wadi Wassat, Saudi Arabia: Saudi Arabian Dir. Gen. Mineral Resources Tech. Record TR-1972-1, 244 p.

Joyce, A.S., and Clema, J.M., 1974, An application of statistics to the chemical recognition of nickel gossans in the Yilgarn Block, Western Australia: Proc. Australas. Inst. Min. Metall., no. 252, p. 21-24.

Nickel, E.H., 1973, Violarite, a key mineral in the supergene alteration of nickel sulphide ores, in Western Australia Conference, 1973, Papers, Precambrian ore genesis: Australas. Inst. Min. Metall., Parkville, Victoria, p. 111-116.

Nickel, E.H., Ross, J.R., and Thornber, M.R., 1974, The supergene alteration of pyrrhotite-pentlandite ore at Kambalda, Western Australia: Econ. Geol., v. 69, p. 93-107.

Nickel, E.H., Allchurch, P.D., Mason, M.G., and Wilmshurst, J.R., 1977, Supergene alteration at the Perseverance nickel deposits, Agnew, Western Australia: Econ. Geol., v. 72, p. 184-203.

Overstreet, W.C., and Rossman, D.L., 1970, Reconnaissance geology of the Wadi Wassat quadrangle, Kingdom of Saudi Arabia: U.S. Geol. Survey open-file rept. (IR)SA-117, 68 p.

Roberts, D.E., and Travis, G.A., 1973, Textural evaluation of nickel sulphide gossans (abs.), in Western Australia Conference, 1973, Papers, Mineral exploration methods: Australas. Inst. Min. Metall., Parkville, Victoria, p. 97.

Roberts, R.J., 1976, The genesis of disseminated and massive sulfide deposits in Saudi Arabia: U.S. Geol. Survey open-file rept. (IR)SA-207, 54 p.

Thornber, M.R., 1975a, Supergene alteration of sulphides.
     I, A chemical model based on massive nickel sulphide
     deposits at Kambalda, Western Australia: Chem. Geol.,
     v. 15, p. 1-14.

_____ 1975b, Supergene alteration of sulphides. II, A
     chemical study of the Kambalda nickel deposits: Chem.
     Geol., v. 15, p. 117-144.

Travis, G.A., Keays, R.R., and Davison, R.M., 1976, Palladium
     and iridium in the evaluation of Ni gossans in Western
     Australia: Econ. Geol., v. 71, p. 1229-1243.

Wilmshurst, J.R., 1975, The weathering products of nickeli-
     ferous sulphides and their associated rocks in western
     Australia, in Elliott, I.L., and Fletcher, W.K., eds.,
     Geochemical exploration 1974: Elsevier, Amsterdam,
     p. 417-436.

HYDROTHERMAL NICKELIAN MACKINAWITE AND
ALABANDITE AT WADI QATAN

Nickelian mackinawite is a common alteration product in nickel sulfide ores (Uytenbogaardt and Burke, 1971), but its association with alabandite is unusual. This section reports the occurrence of nickelian mackinawite associated with pentlandite and alabandite and discusses a possible mechanism for its formation.

At Wadi Qatan, a lens of rock mineralized by fine-grained pyrrhotite-pentlandite and pyrite-pentlandite lies conformably within a sequence of metamorphosed basaltic and andesitic rocks intruded by granite and diorite. Field and textural evidence indicate that the pyrrhotite is probably derived from pre-existing pyrite by contact metamorphism, and that much of the pyrrhotite so-formed has been locally re-pyritized (Blain, in press). The resultant assemblages consist of pyrite or pyrrhotite with pentlandite and minor amounts of chalco-pyrite, cubanite, alabandite, and molybdenite. Nickelian mackinawite, as an alteration product, has two modes of occurrence: (i) pentlandite ⟶ nickelian mackinawite + carbonate, and (ii) alabandite ⟶ nickelian mackinawite + carbonate. All stages of alteration from incipient (fig. 5 a) to partial (fig. 5 c) and total (fig. 5 b) replacement are present. The nickelian mackinawite, derived from both pent-landite and alabandite, consists of a delicately interwoven, fibrous mat of crystals. It is generally porous in appearance,

29
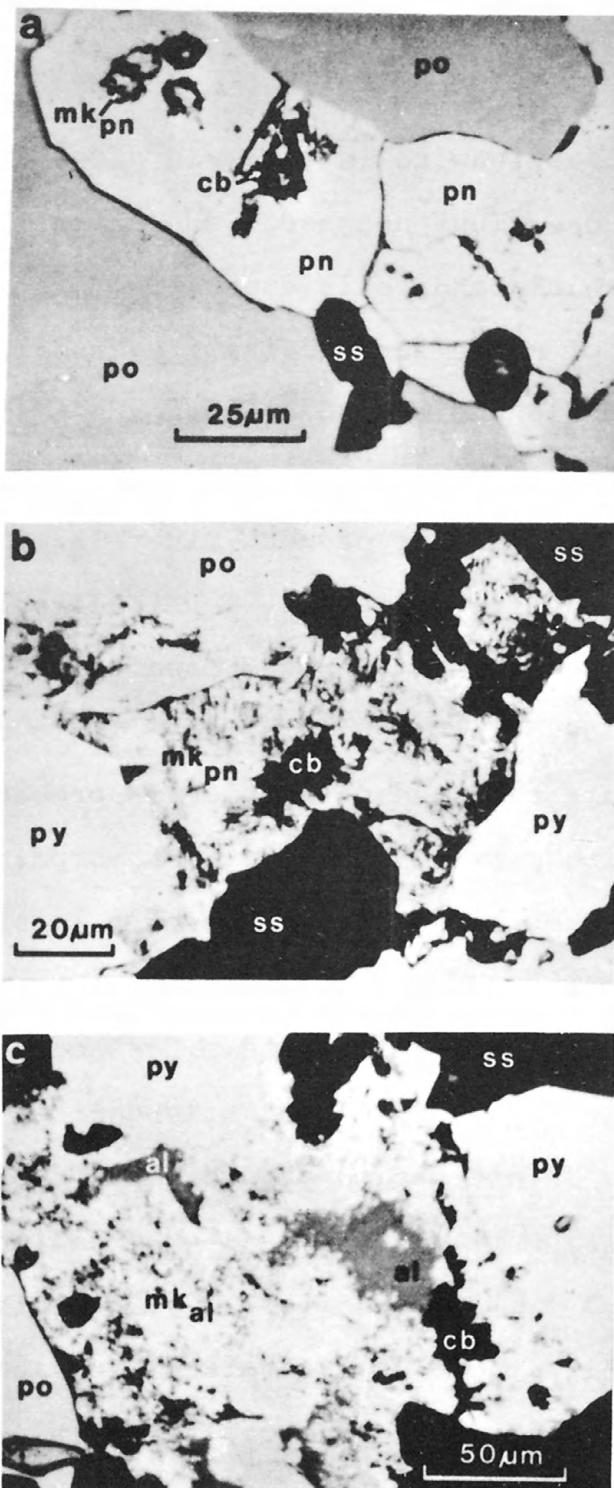
Figure 5. Photomicrographs illustrating the alteration of pentlandite (fig. 5a, b) and alabandite (fig. 5c) to nikelian mackinawite and carbonate. Mineral abbreviations are: pn - pentlandite, po - pyrrhotite, py - pyrite, al - alabandite, mk - nickelian mackinawite, cb - carbonate, ss - silicate; the subscript denotes the replaced mineral. All photographs were taken in plane polarized reflected light under oil immersion.

indicating a volume reduction in the reaction. The associated carbonate minerals form in discrete clusters and are generally less abundant than the mackinawite. In places, the alteration is associated spatially with cross-cutting veinlets of pyrite. The association, mode of occurrence, and textures suggest that the alteration is hydrothermal.

Electron probe micro-analysis data on the alteration (table 1) indicate the following approximate compositions: pentlandite ($Fe_{4.8}Ni_{4.2}S_8$), alabandite (Mn S), nickelian mackinawite ($Fe_{0.7}Ni_{0.3}S$), and carbonate phase (estimated $Fe_{0.6}Mn_{0.4}CO_3$). Assuming that the hydrothermal alteration takes place with a constant sulfur content, the general reactions involved may be expressed as follows:

$$(1) \quad 0.125\ Fe_{4.8}Ni_{4.2}S_8 + 0.1\ Fe^{++} \longrightarrow Fe_{0.7}Ni_{0.3}S + 0.225\ Ni^{++}$$

pentlandite $(257.2/8 = 32.15\ Å^3)$ nickelian mackinawite $(33.67\ Å^3)$

$$(2) \quad Mn\ S + 0.7\ Fe^{++} + 0.3\ Ni^{++} \longrightarrow Fe_{0.7}Ni_{0.3}S + Mn^{++}$$

alabandite $(35.63\ Å^3)$ nickelian mackinawite $(33.67\ Å^3)$

$$(3) \quad 0.6\ Fe^{++} + 0.4\ Mn^{++} + 2HCO_3^{-} \longrightarrow Fe_{0.6}Mn_{0.4}CO_3 + CO_2 + H_2O$$

rhodocrosite - siderite $(49.80\ Å^3)$
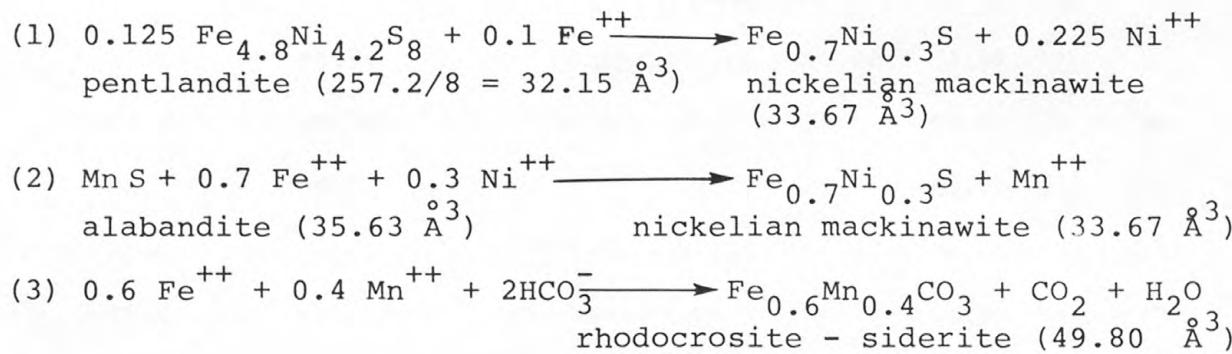
The slight increase in molecular volume (in parentheses) for reaction (1) is inconsistent with the textural evidence of volume reduction and so it is quite possible that the actual reaction might also involve removal of some of the sulfur from the site of alteration. Nevertheless, the general pattern of elemental gain or loss during alteration is probably portrayed reasonably well by the equations. A feature common to all three equations is that the alteration requires an overall addition of iron. The metals released (nickel and manganese),

31

Table 1.--Elemental composition, in percent, of pentlandite, alabandite, nickelian mackinawite (after pentlandite and alabandite), and associated carbonate phase: selected data obtained by electron probe micro-analysis.

	pentlandite		alabandite		nickelian mackinawite after pentlandite	
Fe	33.36	33.50	5.55	5.06	41.32	42.09
Mn	<0.01	<0.01	58.60	57.60	0.05	0.34
Ni	30.63	31.26	0.22	0.08	19.70	19.86
S	32.31	33.20	36.97	37.30	35.24	33.48
Others	nd[1/]	nd	0.13	0.01	nd	nd
Total	96.30	97.96	101.47	100.05	96.31	95.77

	nickelian mackinawite after alabandite				carbonate phase[2/]	
Fe	40.61	50.09	43.15	43.87	27.34	25.27
Mn	0.69	0.38	0.32	0.30	14.49	16.55
Ni	19.05	12.26	17.21	16.55	1.95	0.88
S	35.36	35.92	36.24	36.14	2.26	0.98
Others	0.13	nd	nd	nd	0.41	0.35
Total	95.84	98.65	96.92	96.86	46.45	44.03

[1/] Not determined.

[2/] These analyses are approximate because the data were corrected as for sulfides. All analyses were performed at the Division of Mineralogy of the Commonwealth Scientific and Industrial Research Organization in Western Australia.

however, appear to be accommodated in the alteration assemblage. Nickel released by the alteration of pentlandite (1) is probably consumed by the formation of nickelian mackinawite from alabandite (2). Manganese released from the alteration of alabandite (2) is probably consumed by the precipitation of the carbonate phase (3). The volumetric proportions of the alteration products empirically suggest that the expelled nickel and manganese are mainly redistributed locally without net removal from the system. It seems likely therefore that alteration is induced by high iron activity, but a mechanism for concentrating iron under these conditions remains problematical.

However, the unusual mode of occurrence of the pyrite and pyrrhotite in this deposit could perhaps be significant. Good evidence suggests that the pyrrhotitic monosulfide was derived from pre-existing pyrite by contact metamorphism. Much of the pyrrhotite so-formed is thought to have been subsequently re-pyritized. Where pyrrhotite is pervasively replaced by pyrite, the overall sulfide fabrics are identical, and no evidence suggests an expansion of the rock mass. The formation of pyrite from pyrrhotite at constant volume theoretically requires the release of some iron:

(4) $\qquad 1.36\ Fe_{0.88}S + 0.64\ S \longrightarrow FeS_2 + 0.2\ Fe^{++}$

pyrrhotite ($1.36 \times 29.25\ \mathring{A}^3 = 39.78\ \mathring{A}^3$) $\quad$ pyrite ($39.75\ \mathring{A}^3$)
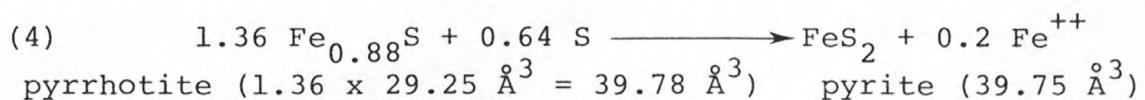
The relatively common association of pyrite with the alteration to nickelian mackinawite and carbonate, especially in the specific case of cross-cutting veinlets, leads to the

speculation that the iron required for this alteration process may be provided by the pyritization of pyrrhotite.

REFERENCES

Blain, C.F., in press, Mineralization and gossans in the Wadi Wassat-Wadi Qatan region, Saudi Arabia: Trans. Instn. Min. Metall.

Uytenbogaardt, W., and Burke, E.A.J., 1971, Tables for microscopic identification of ore minerals, 2nd revised edition: Elsevier, London, p. 140.