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METAMORPHISM AND SUPERGENE ALTERATION OF Cu–Ni SULFIDES, THIERRY MINE, NORTHWESTERN ONTARIO*

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ABSTRACT

Four principal types of sulfide ore are recognized at the Thierry mine, located in the Uchi volcanic belt (Superior Province), northwestern Ontario. These are: disseminated Cu–Ni–Fe sulfides, breccia ore, mylonite ore and bornite ore. The sulfides are interpreted to be of magmatic origin, but modified by strong shearing to produce mylonite and breccia ore. The bornite ore represents enrichment in Cu of blocks of amphibolite schist in the mylonite. Supergene alteration removed iron from the iron–nickel sulfides to produce iron oxides and sulfides, especially violarite enriched in cobalt and nickel. Violarite (Ni–Fe-rich) appears to coexist with pentlandite where it formed from pentlandite. Violarite (Ni–Co-rich) generated as the result of metamorphism does not coexist with pentlandite. This strongly suggests that cobalt plays a major role in defining the low-temperature stability fields and explains the two conflicting interpretations of assemblages involving violarite in the system Fe–Ni–S. The modification, during deformation and metamorphism, of primary magmatic sulfides of subeconomic grade to an ore deposit at Thierry and other areas implies that an ultramafic–gabbroic body in an intensely metamorphosed and deformed terrane might offer a better target for exploration than ore in lower-grade rocks. Furthermore, the enrichment of platinum-group elements (PGE) in mylonite and bornite ores at Thierry indicates that mobilization into shear zones could produce PGE deposits.

Keywords: copper–nickel sulfides, metamorphism, deformation, platinum-group elements, supergene alteration, Thierry mine, Ontario.

SOMMAIRE

On reconnaît quatre types principaux de sulfures à la mine Thierry, située dans la ceinture volcanique d'Uchi (province du Supérieur), dans le Nord-Ouest de l'Ontario. Ce sont: les sulfures disséminés de Cu–Ni–Fe, le minerai bréchifié, le minerai mylonitisé et le minerai de bornite. Les sulfures sont considérés comme étant d'origine magmatique; ils ont été modifiés par un cisaillement intense qui a produit le minerai des types mylonitisé et bréchifié. Le minerai de bornite représente un enrichissement en cuivre des blocs de schiste amphibolitique inclus dans la mylonite. L'altération supergène a déplacé le fer des sulfures de fer–nickel pour former des oxydes et des sulfures de fer, en particulier la violarite enrichie en cobalt et en nickel. Une violarite riche en Ni–Fe semble coexister avec la pentlandite là où elle s'est formée à ses dépens. Par contre, la violarite riche en Ni–Co due au métamorphisme ne coexiste pas avec la pentlandite. Le cobalt jouerait donc un rôle clé dans la définition des champs de stabilité à basse température et expliquerait les deux interprétations contradictoires des assemblages impliquant la violarite dans le système Fe–Ni–S. La transformation de minéralisations sub-économiques en gîtes économiques, à Thierry et ailleurs, reliée à la déformation et au métamorphisme des sulfures magmatiques, implique qu'un massif ultramafique – gabbroïque pourrait offrir de meilleures chances de succès à l'exploration dans un terrain intensément métamorphisé et déformé que dans un autre moins métamorphisé. De plus, l'enrichissement des éléments du groupe du platine (EGP) dans le minerai mylonitisé et celui de bornite à la mine Thierry montre que la mobilisation dans des zones de cisaillement pourrait donner naissance à des dépôts d'EGP.

(Traduit par la Rédaction)

Mots-clés: sulfures de Cu–Ni, métamorphisme, déformation, éléments du groupe du platine, altération supergène, mine Thierry, Ontario.

INTRODUCTION

The purpose of this paper is to document and explain the various sulfide assemblages at the Thierry mine. Interpretation of these, in conjunction with the petrographic study of the host rocks, illustrates that copper–nickel deposits associated with mafic to ultramafic rocks are not static after their formation by magmatic processes (Patterson 1980, Patterson & Watkinson 1984). Rather, dynamic regional metamorphism and supergene alteration can play a major role in the development of ore bodies associated with these rocks.

The Thierry mine, owned by Umex Inc., is located in the Uchi volcanic belt, Superior structural province, 450 km northwest of Thunder Bay, Ontario, near the town of Pickle Lake (Patterson & Watkinson 1984, Fig. 1). The geological setting of the mine and surrounding area is described in detail in the preceding paper (Patterson & Watkinson 1984; see especially Fig. 3).

TYPES OF Cu–Ni SULFIDE ORE

At the Thierry mine, there are four principal types

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of sulfide: disseminated sulfides, breccia ore, mylonite ore and bornite ore, making up <1%, 40%, 58%, and <1%, respectively, of the sulfides mineral assemblages. The disseminated sulfides occur in thick sections of mafic metagabbro and talc–carbonate schist. Breccia ore occurs as irregular zones in faults within the mafic metagabbro and mylonite (chlorite–biotite schist). Breccia ore grades into mylonite ore, which occurs in the main northwest-trending shear zone. The bornite ore occurs in

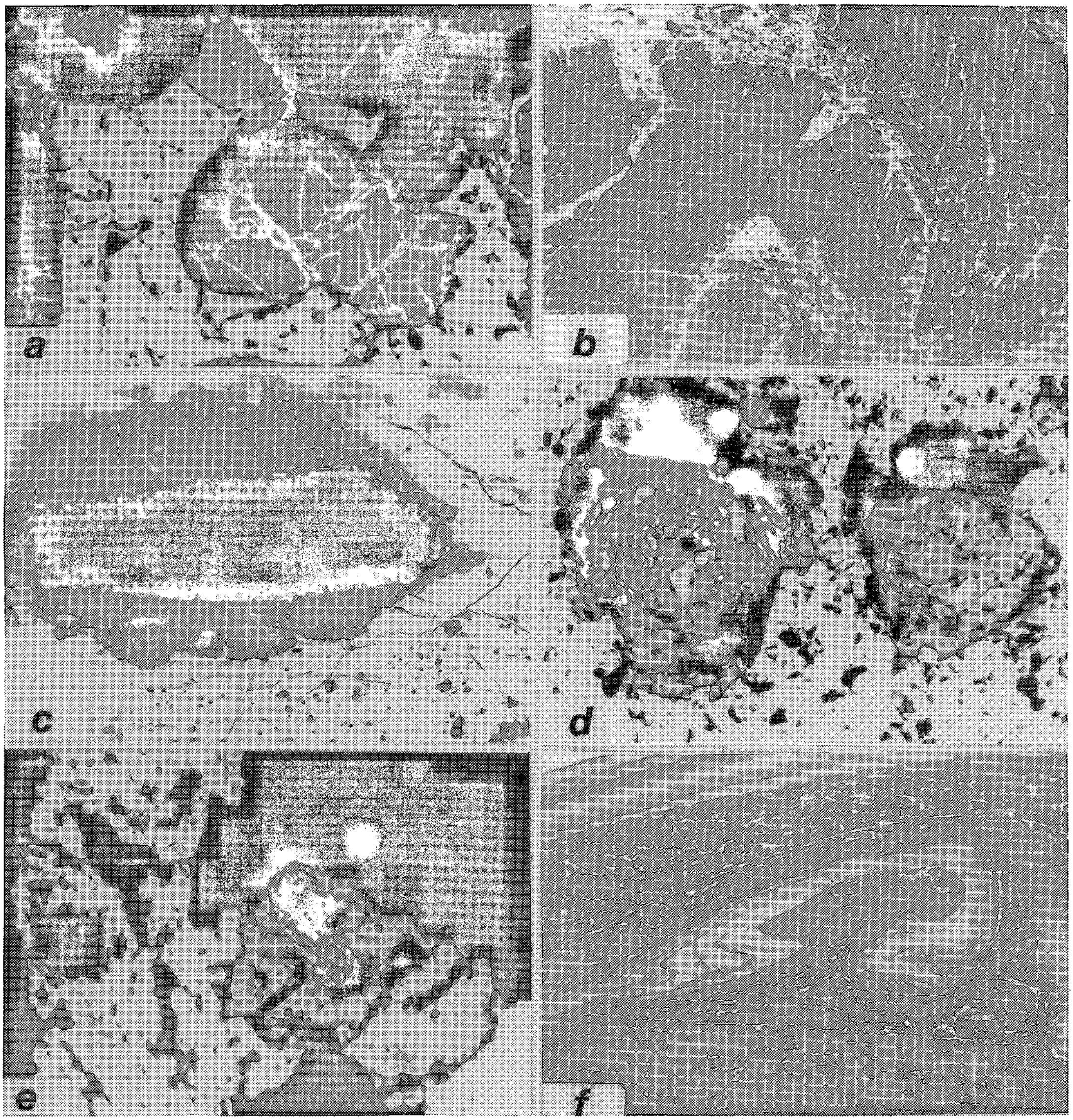

FIG. 1. a. Disseminated sulfides; chalcopyrite, pyrrhotite (light grey) and magnetite (medium grey) intercumulus with respect to olivine (partly altered to serpentine); specimen K9-208. Field of view 5.6 mm. b. Breccia ore; metagabbro fragments with sulfides penetrating along fractures; specimen TH–14, west pit, 2nd bench. Field of view 8.5 cm. c. Breccia ore; a fragment of metagabbro rimmed by pyrrhotite (dark grey) in a matrix of chalcopyrite (white), 600 crosscut. Field of view 14 cm. d. Breccia ore; magnetite crystal with a spiral arrangement of sulfide and silicate inclusions. 4–032–153. Field of view 1.2 cm. e. Altered breccia ore; dendritic pyrite (white) after pyrrhotite with spongy violarite (grey). 600–IE–HOR–65. Field of view 2.1 mm. f. Mylonite ore; highly folded and deformed fragments of wallrock. Pyrrhotite and chalcopyrite occur as fine disseminations stretched parallel to the foliation. West pit, 2nd bench. Field of view 8.5 cm.

TABLE 1. AVERAGE COMPOSITION OF SULFIDES FROM THE THIERRY MINE: DISSEMINATED ORE AND BORNITE ORE

DISSEMINATED ORE	NO. OF GRAINS	WEIGHT PERCENT S	Bi	Fe	Co	Ni	Cu	TOTAL	FORMULA
bornite	3	26.9	-	14.8	Tr	-	58.1	99.8	$Cu_{4.35}Fe_{1.26}S_4$
cubanite	3	35.4	-	40.1	-	-	24.8	100.3	$Cu_{1.06}Fe_{1.95}S_3$
pyrrhotite	3	36.6	-	62.6	-	-	-	99.2	$M_{7.84}S_8$
pentlandite	3	32.6	-	27.5	9.13	29.8	1.55	100.6	$M_{9.2}S_8$
BORNITE ORE									
millerite	4	34.7	-	1.44	5.40	58.3	1.69	101.5	$M_{1.05}S$
carrollite	3	38.5	-	0.99	33.6	11.3	10.9	95.3	$M_{2.95}S_4$
bornite	2	25.2	-	14.1	n.d.	n.d.	60.8	100.1	$Cu_{4.86}Fe_{1.27}S_4$
wittichenite	1	19.2	43.2	n.d.	-	-	38.4	100.8	$Cu_{2.9}BiS_{2.9}$
emplectite	1	19.2	61.0	n.d.	-	-	19.4	99.6	$CuBiS_2$

Tr trace, n.d. not detected, n.a. not analyzed

metavolcanic blocks included in the mylonite (Patterson & Watkinson 1984, Fig. 3). Representative chemical compositions of sulfides and precious-metal minerals are presented in Tables 1–5; textural relationships are illustrated in Figures 1 and 2.

Disseminated sulfides

Disseminated sulfides consist of two types, those intercumulus to magmatic silicates (Fig. 1a) and those that have been modified during the formation of metamorphic silicates, and are now disseminated along cleavages in amphibole and chlorite. Both types consist of chalcopyrite, pyrrhotite, pentlandite, bornite and cubanite intergrown with magnetite; the sulfides are compositionally similar in the two groups (Table 1).

Cobalt-rich pentlandite occurs as exsolution flames and pods in pyrrhotite. Rare emulsion-textures consist of pentlandite and chalcopyrite. The pentlandite shows minor alteration to mackinawite. Cubanite occurs as distinct lamellae in chalcopyrite.

Breccia ore

Breccia ore is composed of 20 to 50% sulfides with 50 to 80% rounded to angular fragments of wallrock. The fragments range from 0.5 cm to 2 m across. The fragments commonly are shattered, with sulfides penetrating the fractures (Fig. 1b). The fragments of wallrock are predominantly mafic metagabbro with minor mafic volcanic rocks and mylonite. The gradation of mylonite to breccia ore, the occurrence of breccia ore in faults and the presence of mylonite fragments in the breccia ore suggest that the breccia formed as a result of the shearing process that formed the mylonite.

The sulfides consist of chalcopyrite, pyrrhotite, pentlandite, irregular violarite after pentlandite, lamellar violarite after pyrrhotite, smythite, pyrite, cobalt-rich pyrite, nickel-rich pyrite, sphalerite, galena, vaesite and mackinawite (Table 2). In unaltered specimens, the breccia ore consists of chalcopyrite, some with pyrrhotite rims as thick as 0.5 cm on fragments (Fig. 1c). Pentlandite occurs as flames and pods on the margins of polygonally recrystallized pyrrhotite (Fig. 2a). Most of the breccia ore shows some degree of alteration (Fig. 1e). The pyrrhotite is altered to smythite and lamellar iron-rich violarite along fractures in the pyrrhotite. Pentlandite is altered to a mixture of nickel- and cobalt-rich violarite and nickel-rich pyrite. Vermiform mackinawite occurs in chalcopyrite. Porphyroblasts of cobalt-rich pyrite are common in chalcopyrite and pyrrhotite.

Magnetite poikiloblastically encloses all sulfides in unaltered specimens. Some of the magnetite crystals contain a spiral trail of inclusions similar to that in snowball garnet (Fig. 1d), suggesting growth and rotation during metamorphism.

The precious-metal minerals in the breccia ore (Table 3) are merenskyite, moncheite, kotulskite, stuetzite and an unknown phase with the composition Ag_3BiTe_2. These are found as small (less than 0.1 mm in diameter) isolated grains with chalcopyrite, pyrrhotite and pentlandite. The moncheite occurs in chalcopyrite, pyrrhotite and pentlandite with small pods of stuetzite. Merenskyite occurs with lamellae of kotulskite and stuetzite. One specimen contains stuetzite intergrown with Ag_3BiTe_2.

Mylonite ore

The sulfide mineralogy of the mylonite ore (Table 4) is very similar to that of the breccia ore into which

TABLE 2. AVERAGE COMPOSITION OF SULFIDES FROM THE THIERRY MINE: BRECCIA ORE

BRECCIA ORE	NO. OF GRAINS	S	Fe	WEIGHT PERCENT Co	Ni	Cu	Zn	TOTAL	FORMULA
pyrrhotite	27	40.5	57.6	0.18	0.96	n.d.	n.d.	99.2	$M_{6.95}S_8$
pyrite (Co-rich)	4	53.7	44.1	2.62	Tr	n.d.	n.d.	100.4	$M_{0.99}S_2$
pyrite (Ni-rich)	11	52.4	43.8	0.25	2.67	n.d.	n.d.	99.1	$M_{1.02}S_2$
smythite	4	40.7	56.6	0.16	1.66	n.d.	n.d.	99.1	$M_{9.03}S_{11}$
pentlandite	6	33.6	26.4	3.20	36.4	0.17	Tr	99.8	$M_{8.8}S_9$
violarite (in pn)	7	41.7	25.9	2.39	27.7	-	-	97.7	$M_{3.01}S_4$
violarite (in po)	9	40.8	28.0	1.55	27.3	-	-	97.7	$M_{3.12}S_4$
sphalerite (in po)	5	32.2	6.22	0.12	0.15	1.5	59.9	100.1	$M_{1.05}S$
sphalerite (with py+po)	1	32.6	7.71	-	-	-	59.9	100.2	$M_{1.03}S$

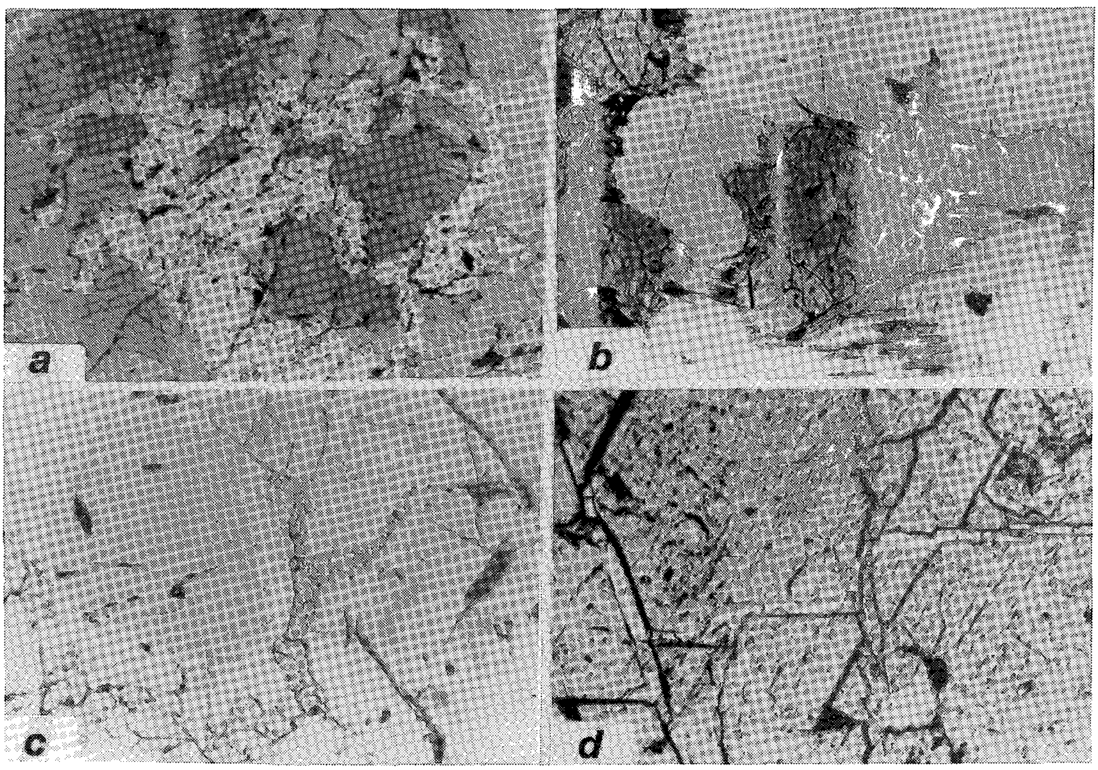

FIG. 2. a. Breccia ore; polygonally recrystallized pyrrhotite (dark grey), flames of smythite (medium grey) and pentlandite exsolved around the margin of the pyrrhotite, West pit, 2nd bench. Field of view 5.6 mm. b. Breccia ore; violarite (dark grey) after pentlandite in a matrix of pyrrhotite (light grey), Th-10. Field of view 5.6 mm. c. Breccia ore; polygonally recrystallized pyrrhotite (dark grey) with flames of smythite (medium grey) and violarite along the margin of the pyrrhotite, Th-9. Field of view 5.6 mm. d. Breccia ore; violarite (grey) after pentlandite, showing octahedral parting of the pentlandite. Nickel-rich pyrite in the shrinkage fractures, specimen Th-9. Field of view 2.1 mm.

TABLE 3. COMPOSITION OF THE PRECIOUS-METAL MINERALS FROM THE THIERRY MINE

	NO. OF ANALYSES	WEIGHT PERCENT AND ATOMIC RATIO									
		S	Te	Bi	Ag	Au	Pd	Pt	Ni	Fe	TOTAL
moncheite	11	n.d.	55.4	7.38	n.d.	n.d.	11.6	22.8	0.93	0.22	98.3
$M_{1.08}(Te,Bi)_2$		–	0.43	0.035	–	–	0.109	0.117	0.016	0.002	
merenskyite[1]	2	n.a.	60.1	8.01	2.12	n.d.	26.0	3.80	n.d.	n.d.	100.0
$M_{1.12}(Te,Bi)_2$		–	0.47	0.038	0.02	–	0.249	0.019	–	–	
merenskyite[2]	1	n.a.	61.1	6.38	9.53	n.d.	16.9	3.52	n.d.	n.d.	97.4
$M_{1.02}(Te,Bi)_2$		–	0.48	0.031	0.088	–	0.155	0.018	–	–	
kotulskite	1	n.a.	53.5	1.80	n.d.	n.d.	44.3	2.31	n.d.	n.d.	101.9
$M_{0.99}(Te,Bi)$		–	0.42	0.009	–	–	0.41	0.012	–	–	
stuetzite[3]	5	n.a.	39.7	Tr	56.8	1.54	0.75	0.38	n.d.	n.d.	99.2
$M_{5.29}Te_3$		–	0.31	–	0.53	0.008	0.007	0.002	–	–	
unknown	2	n.a.	33.0	25.7	40.1	n.a.	n.d.	n.d.	0.57	n.d.	99.4
Ag_3BiTe_2		–	0.26	0.13	0.37	–	–	–	0.01	–	
acanthite[4]	1	13.4	n.d.	Tr	87.0	n.d.	n.a.	n.a.	n.a.	n.a.	100.7
$Ag_{1.93}S$		0.42	–	–	0.81	–	–	–	–	–	
native silver	1	n.d.	n.d.	n.d.	97.8	2.1	n.a.	n.a.	n.a.	n.a.	99.9
(Ag, Au)		–	–	–	0.91	0.11	–	–	–	–	

1. exsolved with kotulskite. 2. exsolved with stuetzite. 3. high std. dev. 4. 0.30% Cu.

it grades, except that it has many deformation textures not present in the breccia ore. The sulfides occur molded around silicate fragments, as stringers penetrating rock and crystal fragments, in pressure shadows and in stringers elongated parallel to the foliation (Fig. 1f). The sulfides tend to occur in the biotite-rich layers of mylonite. Ductile sulfides such as chalcopyrite and pyrrhotite tend to occur in thin veinlets and in pressure shadows of silicate fragments and cobalt-rich pyrite crystals. Magnetite occurs as euhedral poikiloblasts in sulfides and as broken and shattered fragments scattered through the matrix of the mylonite.

Chalcopyrite shows deformation twins; pyrrhotite is polygonally recrystallized, and deformation twins are common. Pentlandite characterized by alteration to violarite occurs as isolated grains and exsolution blebs along grain boundaries in pyrrhotite. The pyrrhotite is altered to smythite and lamellar violarite.

Bornite ore

Within the mylonite, there are blocks as large as 20 m in diameter of mafic metavolcanic rocks (amphibolite schist). The bornite ore occurs as disseminations and in carbonate veins within these blocks. The sulfides make up 2 to 3% of the rock.

The ore minerals are intergrown chalcopyrite and bornite with copper–bismuth sulfosalts (wittichenite and emplectite). Native silver (with acanthite and stuetzite) and rare merenskyite occur as small disseminated grains within bornite or chalcopyrite (Table 3).

Metamorphism of the Thierry Ores

Metamorphic textures and structures

Both regional and dynamic metamorphism affected the Cu–Ni sulfides in the Thierry deposit. The effect of regional metamorphism is illustrated by the disseminated ores, in which primary intercumulus sulfides were modified to disseminations along cleavages in amphibole and chlorite. Pyrrhotite commonly forms polygonal crystals showing exsolution of pentlandite along grain boundaries, suggesting that monosulfide solid-solution was formed during metamorphism. This is consistent with results of geothermometry and geobarometry, which suggest that regional metamorphism attained temperatures in the range of 600 to 650°C and pressures from 6.5 to 7 kbar (Patterson 1980).

Dynamic metamorphism produced many purely mechanical effects; sulfides were forced into fractures and pressure shadows, deformation twins were developed, and magnetite rotated. The occurrence of mylonitic fragments in the breccia ore and the gradation of breccia ore into mylonitic ore demonstrate that the breccia ore was formed as a result of dynamic metamorphism.

Chemical effects of metamorphism

The second major effect of dynamic metamorphism is reflected in the bulk composition of the sulfides. The copper-to-nickel ratio in sulfides associated with gabbroic intrusive complexes is normally less than 3 (Naldrett & Cabri 1976). This is the same value as found in the disseminated sulfides of the Thierry mine and in the sulfides associated with other less deformed mafic intrusive bodies in the area (Patterson 1980). However, in the breccia ore and mylonite ore, the copper-to-nickel ratio varies from 5 to 50, averaging 10.5. Furthermore, the bulk mineralogy of the mylonite and breccia ore is unusual, approximately 50% chalcopyrite and 50% pyrrhotite + pyrite, compared to 10% chalcopyrite and 90% pyrrhotite + pyrite in the

TABLE 4. AVERAGE COMPOSITION OF SULFIDES FROM THE THIERRY MINE: MYLONITE ORE

MYLONITE ORE	NO. OF GRAINS	S	Fe	Co	Ni	Cu	Zn	TOTAL	FORMULA
		WEIGHT PERCENT							
pyrrhotite	15	40.4	58.7	0.12	0.75	-	-	100.0	$M_{6\cdot76}S_8$
pyrite (Ni-rich)	3	53.5	45.5	0.14	1.97	-	-	101.1	$M_{1\cdot01}S_2$
pyrite (Co-rich)	7	53.7	44.5	2.71	Tr	-	-	100.9	$M_{1\cdot02}S_2$
pentlandite	3	36.9	26.6	0.44	34.3	-	-	98.2	$M_{8\cdot4}S_9$
violarite (in pn)	5	39.9	27.2	1.44	27.2	-	-	95.7	$M_{3\cdot12}S_4$
sphalerite (with po+py)	2	31.6	7.56	-	-	Tr	60.4	99.6	$M_{1\cdot05}S$

sulfides of other gabbroic complexes.

There are several methods by which sulfides may become enriched in chalcopyrite relative to pyrrhotite and pentlandite. Craig & Kullerud (1969) studied the system Fe–Ni–Cu–S at 1000°C and showed that a copper-rich liquid coexists with monosulfide solid-solution (*Mss*). This might be a reasonable explanation for the Thierry ore if the sulfide could segregate from *Mss* and the silicate magma. However, in a filter-press model, the early precipitation of olivine, pyroxene and plagioclase would probably lock any immiscible sulfide droplets between these silicates, making it difficult for such a copper-rich liquid to separate from the solid sulfides and silicates. If the sulfide magma formed a massive unit, it is unlikely that a copper-rich liquid could migrate because the density contrast between the liquid and the *Mss* would be small. A similar argument could be made for generation of Cu-rich liquid in a system containing oxygen, in which iron oxide and iron–nickel sulfides would solidify, leaving a copper-rich liquid.

Bowdidge (1970) suggested that the copper-rich sulfides at the Thierry mine were generated from the solidification of a magma that was sulfur-deficient. The nickel and iron would have been concentrated in olivine and pyroxene structures, enriching the remaining magma in copper. When the magma became saturated in sulfur, sulfide liquid enriched in copper would precipitate from a magma depleted in nickel and iron. However, the ratio of barren mafic intrusive rock to ore-bearing rocks at the Thierry mine is very low; virtually all the mafic intrusive rocks contain sulfides.

Verbeek *et al.* (1972) mentioned that dynamic metamorphism played an important role in redistributing the sulfides at Thierry. The main contrast between the Thierry mine ultramafic rocks containing ore and the other Kapkichi ultramafic rocks containing subeconomic amounts of sulfide is the amount of shearing and mylonitization. Barrett *et al.* (1977) suggested that most economic concentrations of iron–nickel sulfides were due to dynamic metamorphism. They stated that: "although Fe–Ni sulfides occur in all metamorphic domains, particularly in the dunitic intrusions, only disseminated deposits have been discovered in greenschist metamorphic domains. The matrix and massive sulfides that now represent economic or subeconomic concentrations of nickel in both volcanic-type and dykelike hosts are confined to amphibolite facies domains. Most deposits occur in mid- to high-amphibolite facies domains of dominantly dynamic style."

Evidence for the mechanical separation of pyrrhotite from pentlandite can be seen on a thin-section scale in the mylonite ore at the Thierry mine. Pentlandite occurs as isolated grains in silicates, rather than as exsolution lamella in pyrrhotite, as might be expected as a result of a magmatic origin. The highly variable Cu/Ni and Ni/Fe ratios (Patterson 1980) are consistent with this. Removal of a copper-rich liquid from *Mss* would leave a nickel-rich residuum, which has not been found at the Thierry mine. This implies that during dynamic metamorphism, copper was selectively mobilized relative to nickel and iron. The bornite ore may represent further mobilization of copper into blocks of amphibolite caught up in the mylonitic zone.

Supergene Alteration

The sulfide ores were intensely faulted and fractured during dynamic metamorphism. Three distinct assemblages of sulfide were developed in these sheared rocks. The average composition of the sulfides in altered ore is provided in Table 5.

The first consists of deep violet porous violarite with octahedral shrinkage cracks after pentlandite (Fig. 2b). Pyrite is partly altered to hematite. All gradations between the violarite–pyrite assemblage and the fresh pyrrhotite–pentlandite assemblage are present (Craig & Higgins 1975). This is similar to alteration at Kambalda (Nickel *et al.* 1974) and Mt. Windarra, Australia (Watmuff 1974). Evidence for

TABLE 5. AVERAGE COMPOSITION OF SULFIDES FROM THE THIERRY MINE: ALTERED ORE

ALTERED ORE	NO. OF GRAINS	S	Fe	Co	Ni	Cu	Zn	TOTAL	FORMULA
		WEIGHT PERCENT							
millerite	3	35.0	0.24	0.69	60.6	0.24	n.d.	96.8	$M_{1.04}S$
polydymite (Co-rich)	4	41.8	8.24	12.8	34.4	Tr	n.d.	97.2	$M_{2.91}S_4$
polydymite (Cu-rich)	3	38.6	7.34	0.91	40.0	10.3	n.d.	97.2	$M_{3.28}S_4$
vaesite	2	51.2	0.16	0.52	48.4	n.d.	n.d.	100.3	$M_{1.05}S_2$
pyrite (Co-rich)	4	54.0	44.72	1.20	n.d.	n.d.	n.d.	99.9	$M_{0.97}S_2$
bornite	2	26.2	6.40	n.d.	n.d.	64.8	n.d.	97.4	$Cu_5Fe_{5.6}S_4$
chalcopyrite	2	34.3	29.66	n.d.	n.d.	36.0	n.d.	100.0	$Cu_{1.06}FeS_2$

reactions involving loss of iron to oxides (Table 6) can be seen in the partly altered breccia ore. The nickel released from the violarization of pentlandite (Table 6, reaction 1) combined with smythite (formed by the breakdown of pyrrhotite, reaction 2) to produce iron-rich violarite (reaction 3). In the partly altered ores, pentlandite contains flecks and lamellae of violarite; these follow the octahedral parting in pentlandite (Fig. 2b). Smythite formed flames in pyrrhotite, and lamellar violarite (Nickel *et al.* 1974) appeared along fractures (Fig. 2c). Continuation of this process would have produced Ni-rich pyrite (Fig. 2d) and violarite rich in cobalt and nickel (reaction 4). At Kambalda, further alteration produced oxides and hydroxides (Nickel *et al.* 1974), but at the Thierry mine, an assemblage containing predominantly vaesite, polydymite, pyrite, bornite and chalcopyrite was generated. Vaesite occurs as irregular masses with cobalt-rich pyrite. Polydymite shows octahedral shrinkage-fractures, implying that it was formed as a result of pentlandite alteration. Bornite developed as rims on chalcopyrite and along shrinkage fractures in polydymite. This suggests that further loss of iron and sulfur produced vaesite (reaction 4). A continuation of this loss produced an assemblage of millerite, polydymite and chalcopyrite (reaction 6). The polydymite is very cobalt-rich (12.8% Co). Millerite occurs as fine laths in chalcopyrite. Associated with this assemblage is malachite, native copper, chalcocite and marcasite along joints and fractures. Hematite and magnetite are common in all assemblages.

Violarization and Low-Temperature Relationships in the System Ni-Fe-S

From the preceding description, it is clear that the system was not closed during the process of violarization. The alteration caused an increase in the Ni/Fe and Co/Fe ratios by removing iron from the sulfide assemblages in the form of oxides. This enrichment may explain some of the unusual nickel-rich deposits, such as the Marbridge mine (Graterol & Naldrett 1971), where a premetamorphic supergene process could have changed the bulk composition of the sulfides to a nickel-rich composition.

In examining natural sulfides in the system Ni-Fe-S, there appear to be two possible low-temperature configurations (Craig & Scott 1974), one with millerite-pyrite and the other with pentlandite-violarite. This apparent contradiction hinges on the stability of violarite. If formed from pentlandite, violarite is more Ni-rich than that formed from pyrrhotite, and equilibrium is thus not attained. This is commonly readjusted during metamorphism. The equilibrium assemblage violarite - millerite - pyrite - magnetite reported at Black Swan (Groves *et al.* 1974) and Marbridge (Graterol & Naldrett 1971) may be explained by the metamorphism of supergene-altered Ni-Fe sulfides.

Kullerud (1969) showed that in general, a thiospinel (violarite) breaks down on metamorphism to NiAs-type and FeS_2-type structures at varying temperatures, depending on compositions:

$$Fe_3S_4 = 2\,Fe_{1-x}S + FeS_2 \quad \text{at } 100°C$$
$$Ni_3S_4 = 2\,NiS + NiS_2 \quad \text{at } 340°C$$
$$Co_3S_4 = 2\,CoS + CoS_2 \quad \text{at } 600°C$$

According to Craig (1971), $FeNi_2S_4$ has an upper-temperature limit of 461°C in the system Ni-Fe-S.

Consider the metamorphism of a violarite at a middle amphibolite grade:

$$(Fe,Ni,Co)_3S_4 = FeS_2 + 2NiS + (Ni,Co,Fe)_3S_4$$

The resulting violarite would be nickel-cobalt-rich and texturally distinct from that generated by an alteration process. The Co-rich violarite reported from Black Swan is unpitted, has a high reflectance and takes a good polish (Groves *et al.* 1974). The

TABLE 6. SCHEMATIC REACTIONS INVOLVING THE GENERATION OF VIOLARITE

1.	$Fe_4Ni_5S_8$ =	$Fe_2Ni_4S_8$	+ Ni^{2+} + $2Fe^{2+}$ + 5e		
	Pentlandite	Violarite I			
2.	$(Fe,Ni)_7S_8$ =	$(Fe,Ni)_8S_{11}$	+ Fe^{2+}		
	Pyrrhotite	Smythite			
3.	$(Fe,Ni)_8S_{11}$ + Ni^{2+} =	$Fe_3Ni_3S_8$			
	Smythite	Lamellar Violarite			
4.	$(Fe,Ni,Co)_3S_4$ =	Fe^{2+} +	$2(Fe,Ni)S_2$ +	$(Ni,Fe,Co)_3S_4$	
	Violarite I		Ni-Pyrite	Violarite III	
5.	$(Ni,Fe,Co)_3S_4$ =	Fe^{2+} +	$(Ni,Fe)S_2$ +	$(Fe,Co)S_2$ +	$(Ni,Co,Fe)_3S_4$
	Violarite III		Vaesite	Co-Pyrite	Violarite IV
6.	$(Fe,Ni,Cu)_3S_4$ =	Fe^{2+} +	NiS +	$(Ni,Cu,Fe)_3S_4$	
	Violarite II		Millerite	Violarite	

violarite generated as a result of the violarization of pentlandite is typically pitted, shows octahedral shrinkage-fractures and takes a poor polish. Violarite forms solid solutions from nickel to cobalt (Tarr 1935) and from nickel to iron (Misra & Fleet 1974) end-members. There does not appear to be complete solid-solution between the cobalt and iron end-members. This casts doubt on the practice, in plots of violarite composition, of evenly distributing cobalt between iron and nickel end-members (Misra & Fleet 1974).

In summary, violarite (Ni–Fe-rich) appears to coexist with pentlandite when it results from the alteration of pentlandite. This may not be an equilibrium assemblage. The Ni–Co-rich violarite generated during metamorphism may be refractory and not readily altered to pentlandite. This strongly suggests that cobalt may play a major role in changing the kinetics of the reactions involved and explains the two conflicting configurations in part of the system Fe–Ni–S.

Conclusions

The ores at the Thierry mine have undergone intense modification after their initial deposition as magmatic sulfides. During regional metamorphism, the primary disseminated sulfides were modified by the recrystallization of the surrounding silicates. Strong dynamic metamorphism mobilized the sulfides into fractures and pressure shadows, and produced deformation twins and rotation of magnetite poikiloblasts in mylonitic and breccia ore. Dynamic metamorphism also significantly changed the copper-to-nickel ratio of the mylonite and breccia compared to disseminated sulfides. The occurrence of fragments of mylonite in the breccia ore suggests that the breccia ore also was formed during dynamic metamorphism. The process of shearing and faulting significantly increased the penetration of groundwater into the ore, allowing its supergene alteration. Supergene alteration proceeded by a process that removed iron from the sulfide, producing nickel–cobalt-rich sulfides and iron oxides. Ni–Fe sulfides are open to the addition of oxygen, which effectively removes Fe from the system in the form of oxides. Work by Eckstrand (1975) on the Dumont serpentinite implies that sulfur also may be removed, generating alloys of Ni–Fe. Equilibrium cannot be assumed when considering stability of phases such as violarite, which is produced during these low-temperature processes. The effect of Co on phase relationships among Ni–Fe–S minerals may also play a major role in stabilizing violarite; this may explain the two configurations of the low-temperature phase relationships shown by Craig & Scott (1974).

The unusual Cu/Ni and chalcopyrite-to-pyrrhotite ratios at Thierry are not unique; for example, other cases with unusual Cu/Ni ratios in deformed rocks are the Cu-rich footwall deposits at Sudbury (Abel *et al.* 1979) and the Shebandowan deposit near Thunder Bay, Ontario (Morton 1982). These may have resulted from dynamic processes similar to those active at the Thierry mine, rather than by the filter-press method or other strictly magmatic processes.

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