Canadian Mineralogist
Vol. 14, pp. 450-461 (1976)

SULFIDE MINERALOGY OF THE MAIN IRRUPTIVE, SUDBURY, ONTARIO

J. M. DUKE* AND A. J. NALDRETT

Department of Geology, University of Toronto, Toronto, Ontario, Canada M5S 1A1

ABSTRACT

Sulfide minerals occur in most rocks of the Main Irruptive but usually constitute less than 0.5 modal percent. Two textural categories of sulfide occurrence are recognized: 1) magmatic and 2) deuteric or metamorphic. The magmatic sulfide grains are polymineralic and occur interstitially to primary silicate minerals whereas the deuteric or metamorphic sulfides are typically monomineralic grains which are localized in microfractures or are intergrown with secondary silicate minerals. Magmatic sulfides are virtually restricted to the lower units of the Main Irruptive (i.e., the Mafic, Quartz-rich and South Range Norites) but secondary sulfides occur in all units. The magmatic grains typically comprise the assemblage monoclinic pyrrhotite+chalcopyrite±pentlandite±pyrite±magnetite, but most of the pyrite and magnetite in these grains was produced by the secondary alteration of primary pyrrhotite. The chalcopyrite/pentlandite and cobalt/nickel ratios of the magmatic sulfide grains in the Main Irruptive are higher than those characteristic of the Sudbury ores suggesting that the ores segregated from, or at least equilibrated with, a less differentiated magma than that which formed the exposed portion of the Main Irruptive. The solubility of sulfur in the Main Irruptive magma is estimated to be about 600 ppm at 1200°C and it is concluded that the magma was either saturated or slightly undersaturated with sulfur at the time of emplacement.

SOMMAIRE

Les minéraux sulfurés se trouvent dans la plupart des roches de l'Irruptif principal, mais n'en représentent généralement que moins de 0.5% (en mode). Les gîtes sulfurés se classent, d'après leur texture, en deux catégories: (1) magmatique; (2) deutérique ou métamorphique. Les sulfures magmatiques se présentent en grains polyminéraliques interstitiels parmi les silicates primaires, tandis que les sulfures deutériques ou métamorphiques sont typiquement sous forme de grains monominéraliques localisés dans des microfractures ou en intercroissance dans les minéraux siliceux secondaires. Les sulfures magmatiques n'apparaissent, pratiquement, que dans les subdivisions inférieures de l'Irruptif principal (le mafique, le riche-en-quartz et les norites de la chaîne du Sud), mais les sulfures secondaires se trouvent dans toutes les unités. Typiquement les grains magmatiques constituent l'association pyrrhotite monoclinique+chalcopyrite ±pentlandite±pyrite±magnétite, mais la pyrite et la magnétite de ces grains résultent, en majeure partie, de la deuxime altération de la pyrrhotite primaire. Les rapports chalcopyrite/pentlandite et cobalt/nickel des grains magmatiques de l'Irruptif principal sont supérieurs à ceux qui caractérisent les minerais de Sudbury; cette observation permet de supposer que les minerais proviennent d'un magma moins différencié que celui qui a formé la portion exposée de l'Irruptif principal, magma dont ils se seraient séparés avec ségrégation ou, du moins, avec lequel ils auraient été en équilibre. On estime à 600 ppm la solubilité du soufre dans le magma de l'Irruptif principal et l'on conclut que le magma était saturé ou faiblement sous-saturé en soufre lors de la mise en place.

(Traduit par la Rédaction)

INTRODUCTION

The Sudbury Irruptive is a large, layered intrusive complex which outcrops as an elliptical ring and is believed to be funnel-shaped in cross-section (Naldrett *et al.* 1970). The nickel-copper sulfide ores are associated with an inclusion-rich suite of rocks known as the sublayer (Souch *et al.* 1969) which is localized around the outer margin of the Irruptive and within dyke-like bodies (offsets) which project into the country rocks. The sublayer rocks are in sharp contact with the base of the Main Irruptive and are thought to have been intruded following emplacement of the Main Irruptive (Naldrett & Kullerud 1967; Hewins 1971). It is now generally accepted that the Sudbury ores formed as immiscible sulfide liquids which separated from a mafic silicate magma. However, it is clear that the molten sulfide did not segregate from the sublayer magma *in situ* but rather was carried in suspension in this magma when it was emplaced (Naldrett & Kullerud 1967). Ultramafic inclusions in the sublayer are believed to be disrupted blocks of a hidden zone of the Irruptive (Naldrett & Kullerud 1967; Rae 1975). The intimate association of these inclusions with the

---

*Present address: Regional and Economic Geology Division, Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario, Canada K1A 0E8.

ore suggests that the ultimate source of the ore was also in the hidden zone.

The Sudbury Irruptive has many features in common with other layered igneous intrusions but the rocks forming the Main Irruptive are unusually rich in silica and potash (Naldrett *et al.* 1972). The chemistry of the Main Irruptive is consistent with its being the result of the differentiation of a tholeiitic magma of mantle origin which had assimilated significant quantities of sialic crustal material. The ultramafic inclusions may have crystallized from the Irruptive magma at an earlier stage in the differentiation, before most of the assimilation had occurred. Assimilation may also have played an important role in the formation of the ores. Irvine (1975) has used arguments based on experimentally determined phase relations in synthetic systems to show how assimilation of felsic material by a mafic magma could cause the magma to become saturated in sulfide. However, three fundamental questions must be answered before a good understanding of the ore genesis will be achieved. First, what is the nature and the extent of the hidden zone of the Irruptive? Second, was the sublayer magma a fresh batch of partial melt from the mantle or was it a fraction of the magma which differentiated to form the Main Irruptive? Third, at what stage in the evolution of the Irruptive did the molten sulfide exsolve from the magma? Some clues to the answer of this final question may be provided by knowledge of the sulfide mineralogy of the Main Irruptive. This paper summarizes the results of a systematic investigation of the mineralogy and textural relationships of the sulfides in 191 samples from the Main Irruptive. In addition, 55 samples have been analyzed for sulfur and an attempt has been made to estimate the solubility of sulfur in the magma which formed the Irruptive.

The general geology of the Sudbury area and the location of samples used in this study are shown in Figure 1. Most of the samples employed by Naldrett *et al.* (1970) and by Gasparrini & Naldrett (1972) in their investigations of the silicate and oxide mineralogy of the Main Irruptive have been re-examined with re-

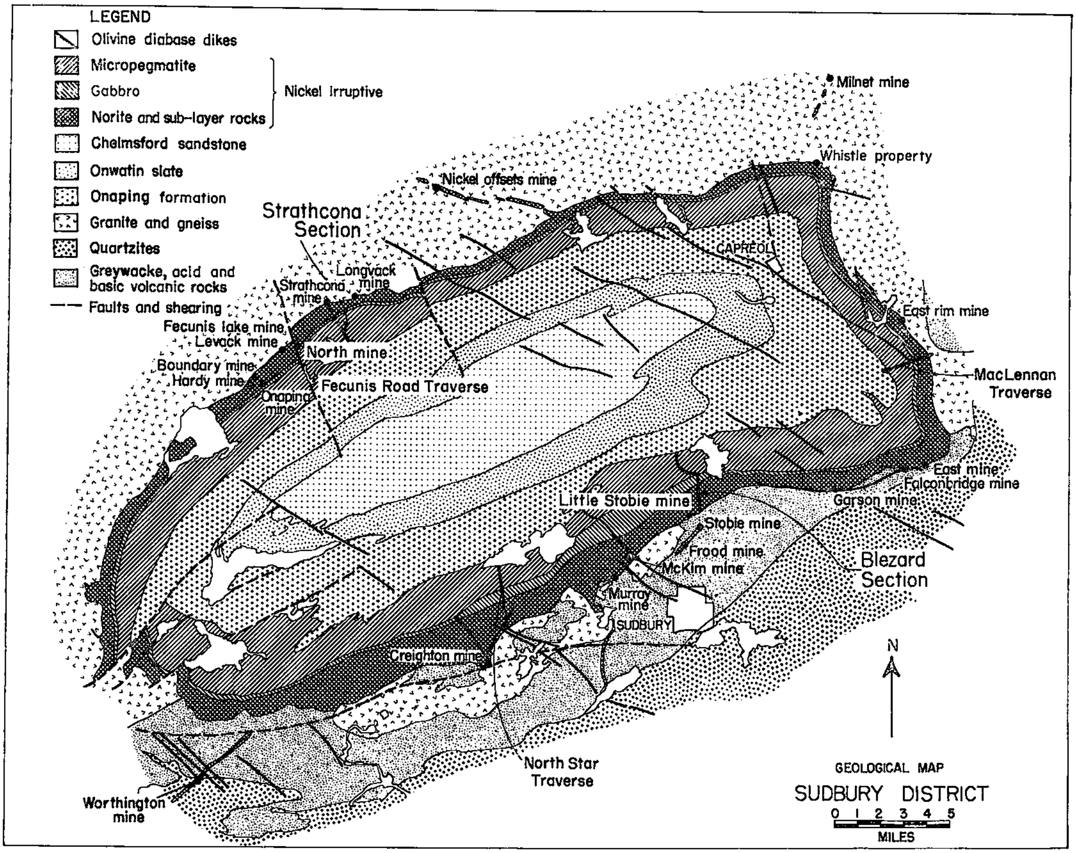

FIG. 1. Geological map of the Sudbury district showing sampling traverses (after Naldrett *et al.* 1970).

gard to their sulfide content. These samples were collected on five traverses across the Irruptive: the North Star (2W series of samples) and Blezard (BL series) sections on the south range, the Maclennan traverse (2R series) on the east range, and the strathcona (M series) and Fecunis Road (FR series) sections on the north range, and the Strathcona (M series) and Fewhich traverse the sublayer — Main Irruptive contact at the Little Stobie mine on the south range (LS series) and at the North mine on the north range (N series).

PETROGRAPHY OF THE MAIN IRRUPTIVE

The geology of the Sudbury Irruptive and associated rocks has been discussed by Hawley (1962), Naldrett & Kullerud (1967), Souch *et al.* (1969), Naldrett *et al.* (1970, 1972), Bray (1972), Gasparrini & Naldrett (1972), Hewins (1974) and Peredery & Naldrett (1975). Only a brief summary of the petrography of the Main Irruptive is given here.

The north and south ranges are petrographically distinct but it is nevertheless possible to draw correlations between them. The modal proportions and compositions of the major minerals in generalized sections through the north and south ranges are presented in Figure 2. The south range above the upper part of the South Range Norite differs only in detail from the north range section above the base of the Felsic Norite, and the Quartz-rich Norite on the south shows a similar reversal in trend of modal proportions as the Mafic Norite on the north range. However, the Quartz-rich Norite is markedly more felsic than the Mafic Norite. There is no correlative on the north range for the lower 4/5 of the South Range Norite.

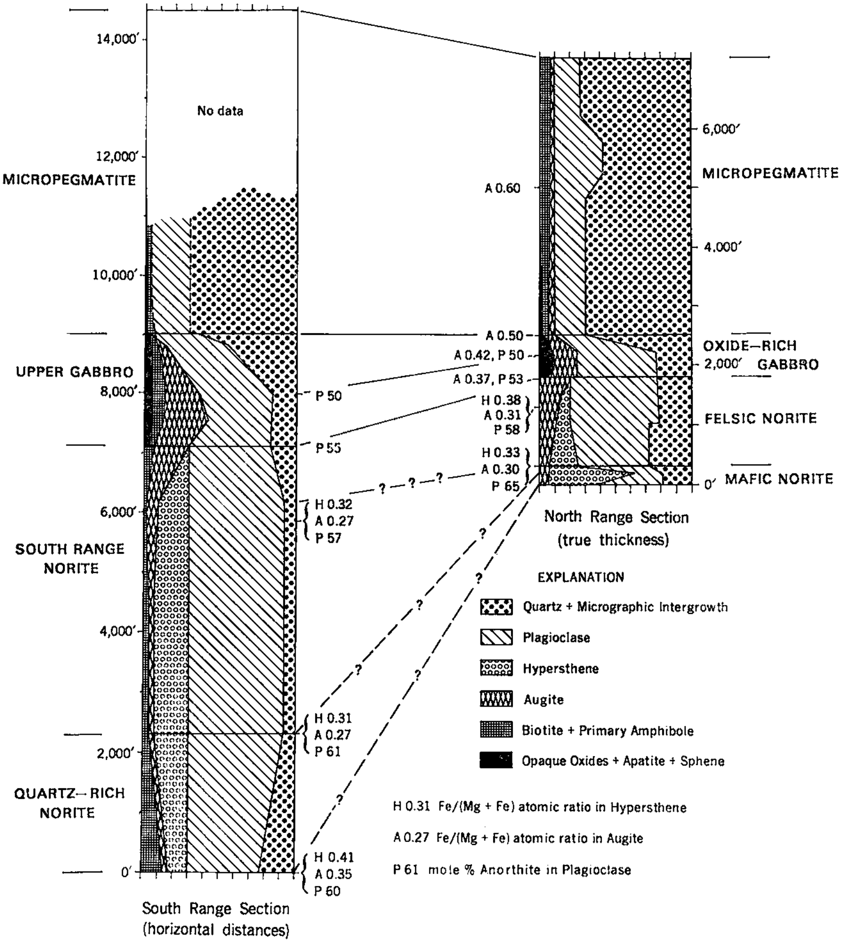

FIG. 2. Classification and correlation of rock units on the north and south ranges of the Main Irruptive (after Naldrett *et al.* 1972).

The presence of cryptic variation, broad-scale phase layering and igneous foliation led Naldrett *et al.* (1970) to suggest that the South Range Norite, Felsic Norite, Upper Gabbro, and Oxide-rich Gabbro are cumulate rocks. Cumulate textures are absent from the Quartz-rich Norite and are present only in the uppermost Mafic Norite (Hewins 1971) and both units are considered to be marginal facies.

SULFIDE MINERALS AND ASSEMBLAGES

More than 90 percent of the samples studied contain microscopically visible sulfide grains although these grains are only occasionally observable in hand specimen. The samples typically contain less than 0.1 modal percent of sulfide minerals but a few specimens from the Mafic Norite and the base of the Quartz-rich Norite have up to 10 modal percent. In order of frequency of observation, the four most common sulfide species in the Main Irruptive rocks are pyrite (py), chalcopyrite (cp), pyrrhotite (po) and pentlandite (pn). Other minerals, including marcasite, violarite, sphalerite and arsenopyrite, were observed in a few samples. This is in contrast to the Sudbury orebodies where pyrrhotite, chalcopyrite and pentlandite are the most abundant phases and pyrite is a relatively minor constituent. Furthermore, cubanite is an important mineral in some of the ores (Hawley 1962) but was not observed in the Main Irruptive samples.

The following five assemblages predominate in the Main Irruptive rocks: (1) po+cp+pn, (2) po+cp+pn+py, (3) po+cp+py, (4) py+cp, (5) py. The frequency of observation of these assemblages in the various rock units is summarized in Table 1. The most common assemblage in the Quartz-rich Norite is po+cp+pn+py, whereas in the lower ¾ of the South Range Norite pentlandite was less frequently observed and po+cp+py is the dominant assemblage. Pyrite is generally the only sulfide mineral present in the upper ¼ of the South Range Norite, the Upper Gabbro and the Micropegmatite. On the north range a sudden transition is observed from the assemblage po+cp+pn in the Mafic Norite to pyrite alone in the Felsic Norite. This is in agreement with the findings of Naldrett & Kullerud (1967) at the Strathcona mine. Pyrite is usually accompanied by a very small amount of chalcopyrite in the Oxide-rich Gabbro, whereas pyrite is commonly the sole sulfide phase in the Micropegmatite. The distribution of sulfide assemblages among the various rock units is generally consistent with the correlation of these units by Naldrett *et al.* (1970, 1972).

TABLE 1. FREQUENCY OF OBSERVATION OF SULFIDE ASSEMBLAGES

Assemblage	Po-Cp-Pn	Po-Cp-Pn-Py	Po-Cp-Py	Py-Cp	Py	Nil or Other
Petrographic Unit						
South Range						
Quartz-rich Norite (29)	0	16	2	5	5	1
South Range Norite (41)	0	7	12	10	9	3
Upper Gabbro (12)	0	1	0	2	3	6
Micropegmatite (7)	0	0	0	0	3	4
North Range						
Mafic Norite (6)	4	2	0	0	0	0
Felsic Norite (21)	0	0	0	1	18	2
Oxide-rich Gabbro (48)	0	0	2	27	17	2
Micropegmatite (27)	0	0	0	0	20	7

Tabulation excludes accessory minerals and supergene alteration products. The numbers in parentheses indicate the number of samples of each rock unit.

The assemblage po+cp±py±pn is characteristic of the lower part of the Main Irruptive and indicates equilibration at low temperatures. Yund & Kullerud (1966) found that pyrrhotite and chalcopyrite react above 334±10°C to form pyrite and "cubanite" (that is, intermediate solid solution; Cabri 1973). The maximum temperature of coexistence of pyrite and pentlandite is 212±13°C (Craig 1973).

TEXTURAL AND COMPOSITIONAL RELATIONSHIPS

Sulfide grains which occur in the Main Irruptive rocks may be categorized on the basis of their textural relationships to the silicate and oxide minerals as follows: 1) magmatic sulfide grains, and 2) deuteric or metamorphic sulfide grains. The magmatic sulfides are found in the Mafic Norite on the north range and in the Quartz-rich Norite and lower part of the South Range Norite on the south range. Deuteric or metamorphic sulfide grains occur in all of the petrographic units of the Main Irruptive.

Magmatic sulfide grains

The magmatic category includes those sulfide grains which initially formed during the magmatic stage of the development of the Irruptive although it is stressed that these grains have been affected to varying degrees by secondary processes. The magmatic sulfides usually comprise blebby, polymineralic grains (Fig. 3A & 3B). The blebs are typically molded about magmatic silicate minerals and are examples of the "interstitial" texture which is common in some of the disseminated Sudbury ores. The external morphology of the blebs and their relationship to the silicates suggests that they formed as immiscible sulfide liquid droplets which did not solidify until much of the engulfing silicate melt had crystallized (Naldrett 1969). If the droplets had solidified before the silicates, the subspherical shape characteristic of the "buckshot" ore texture would have been

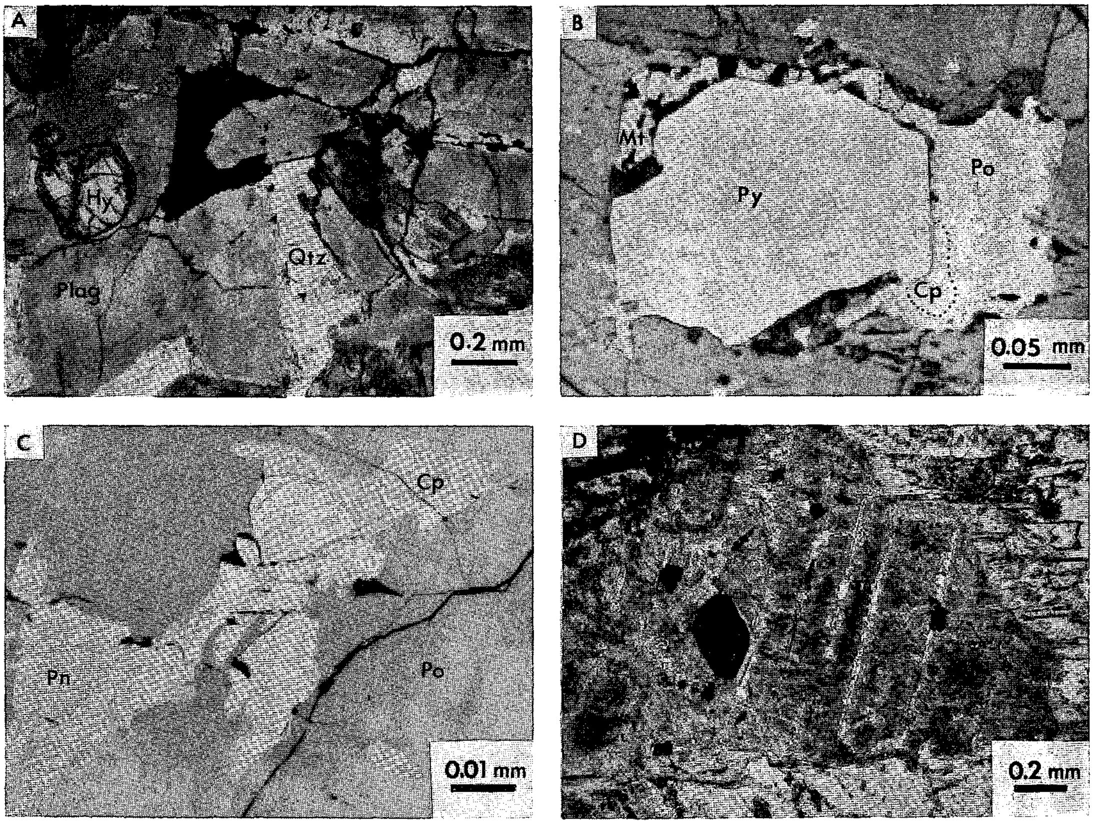

FIG. 3. (A) Sulfide grain (black) displaying interstitial, magmatic texture. Transmitted light. (B) Magmatic sulfide texture; note the association of pyrite (Py) and magnetite (Mt) which are believed to be products of post-magmatic alteration. Reflected light. (C) Typical occurrence of pentlandite (Pn) as both equant grains and as flame-like exsolution in pyrrhotite (Po). Reflected light, oil immersion. (D) Deuteric or metamorphic sulfide texture. Intergrowth of pyrite (black) with secondary amphibole (dark grey) and quartz (white lamellae) which together pseudomorphously replace primary magmatic pyroxene. Transmitted light.

retained. No blebs of magmatic sulfide included entirely within single crystals of primary silicate have been observed. The blebs are typically from 0.1 to 1 mm in size although rare examples up to 10 mm have been observed towards the base of the Main Irruptive. The rocks in which these magmatic sulfides occur typically contain less than about 0.05 wt. % sulfur. Thus a single grain having a volume of 1 mm^3 would contain all the sulfur present in 2000 mm^3 or more of rock. The magmatic blebs do not tend to be associated with the late intercumulus silicates such as biotite and micrographic intergrowth but rather occur interstitially to cumulus plagioclase and hypersthene (Fig. 3A). The concentration of sulfur into a few relatively large grains and the textural relationships between the sulfides and silicates suggest that sulfide droplets exsolved from the magma at an early stage in the crystallization of the latter.

The modal proportions of the various minerals in 12 magmatic grains were determined by point counting (Table 2). Pyrite and pyrrhotite are the most abundant phases except in

TABLE 2. MODAL COMPOSITION OF MAGMATIC-TEXTURED SULFIDE GRAINS

	Po	Cp	Pn	Py	Mt	Po+Py+Mt
Mafic Norite						
Sample N274	82.6	9.2	8.2	0.0	0.0	82.6
Sample N227	80.6	7.4	12.0	0.0	0.0	80.6
Sample N155	77.6	13.2	9.2	0.0	0.0	77.6
Quartz-rich Norite						
Sample LS207	80.6	11.4	5.7	2.3	0.0	82.9
Sample BL5	90.0	8.1	1.9	0.0	0.0	90.0
Sample 2W361	76.2	7.0	0.1	14.4	2.4	93.0
Sample BL79a	6.3	3.5	0.0	50.1	40.1	96.5
Sample BL79b	3.4	11.2	0.0	62.4	23.0	88.8
South Range Norite						
Sample 2W481	55.2	7.2	2.0	32.8	2.8	90.8
Sample 2W531a	22.7	3.3	0.0	66.8	7.2	96.7
Sample 2W531b	0.0	0.7	0.0	83.3	16.0	99.3
Sample BL65	59.8	0.9	2.1	33.3	4.0	97.1

the Mafic Norite and towards the base of the Quartz-rich Norite where pyrite is a minor constituent. An argument will be developed below to the effect that most of the pyrite in the magmatic grains is in fact of post-magmatic origin. Chalcopyrite is almost always present and occurs either at the margins of the blebs or at the boundary between pyrite and pyrrhotite (Fig. 3B), although a few examples of chalcopyrite lamellae in pyrrhotite were observed. Another characteristic mode of occurrence of chalcopyrite is as minute grains disseminated in the silicate matrix in the vicinity of the larger blebs. Pentlandite is present both as flames or lamellae within pyrrhotite and as equant grains localized along pyrrhotite crystal boundaries (Fig. 3C). Pyrite always has an idioblastic relationship to the other sulfide phases within the blebs but conforms to the irregular or curved external outlines of the grains. Magnetite is a common constituent of the pyrite-bearing blebs but was uncommon in pyrite-free grains. Moreover, magnetite almost always occurs in contact with pyrite in preference to the other sulfides (Fig. 3B). Coexisting sulfides from seven magmatic grains were analysed using the electron microprobe and the results are presented in Table 3.

TABLE 3. MICROPROBE ANALYSES OF SULFIDE MINERALS

		Weight Percent						Atomic Percent				
		Fe	Ni	Co	Cu	S	Sum	Fe	Ni	Co	Cu	S
1	Po	59.2	0.5	*	*	39.8	99.5	45.9	0.4	*	*	53.7
	Pn	29.2	34.1	2.4	*	32.7	98.4	24.2	26.8	1.8	*	47.1
	Cp	29.8	*	*	35.8	33.8	99.4	24.8	*	*	26.2	49.0
2	Po	58.6	1.2	0.2	**	39.3	99.3	45.7	0.9	0.2	**	53.2
	Vi	25.1	27.8	3.7	**	38.9	95.5	20.4	21.6	0.9	**	55.1
	Py	43.5	*	3.2	**	52.9	99.6	31.4	*	2.2	**	66.5
3	Po	59.3	0.8	*	*	39.5	99.6	46.0	0.6	*	*	53.4
	Pn	28.7	35.6	2.5	*	33.0	99.8	23.4	27.6	2.0	*	47.0
	Py	44.2	*	2.2	**	52.4	98.8	32.2	*	1.5	**	66.3
4	Po	59.1	0.5	*	*	40.3	99.8	45.4	0.6	*	*	54.0
	Pn	29.4	35.5	1.2	*	33.2	99.3	24.1	27.6	1.3	*	47.3
	Cp	29.6	*	*	35.6	35.3	100.5	24.2	*	*	25.6	50.2
5	Po	58.4	1.1	*	*	39.7	99.2	45.4	0.8	*	*	53.8
	Vi	31.2	23.0	1.1	*	38.5	93.8	25.7	18.1	0.9	*	55.3
	Py	46.0	*	0.6	**	52.8	99.4	33.2	*	0.4	**	66.4
6	Po	58.9	0.8	*	*	39.4	99.1	45.8	0.6	*	*	53.6
	Gr	50.7	1.8	*	*	42.7	95.3	40.0	1.4	*	*	58.6
7	Po	58.6	0.8	*	*	39.3	98.7	45.8	0.6	*	*	53.6
	Vi	25.8	27.2	3.4	0.5	40.0	96.9	20.7	20.7	2.5	0.3	55.7
	Cp	29.8	*	*	33.2	34.1	97.1	25.2	*	*	24.6	50.2

(1) Mafic Norite, Sample N274. (2) Quartz-rich Norite, Sample LS193. (3) Quartz-rich Norite, Sample LS207. (4) Quartz-rich Norite, Sample 2W251. (5) South Range Norite, Sample 2W481. (6) South Range Norite, Sample 2W531. (7) South Range Norite, Sample BL86.

*Element analyzed but not detected. **Element not analyzed.

The mineral analyses were obtained using an ARL electron microprobe operated in the wavelength dispersive mode. Synthetic single crystals of FeS_2, NiS_2 and CoS_2 were used as standards for iron, nickel, cobalt and sulfur, and pure copper metal was used as the standard for copper. The intensity data were corrected using the EMPADR VII procedure. The lower limits of detection of nickel, cobalt and copper were about 0.1 wt. %. The concentrations of sulfur in the seven analyzed pyrrhotites were in the range 53.3 to 54.0 at. % which is very close to the 53.5 at. % expected for monoclinic pyrrhotite coexisting with pyrite at low temperature (Kissin 1974). Several samples were etched with $(NH_4)_2Cr_2O_7$ staining solution but only one pyrrhotite phase was observed. Although the presence of hexagonal pyrrhotite is not precluded, the monoclinic species is apparently predominant in these samples. The iron, nickel and sulfur contents of the pentlandites are very consistent and do not differ significantly from the averages for pentlandites in pn+po+py assemblages compiled from a number of sources in Table 4. The Main Irruptive pentlandites are richer in cobalt than those from other sources. Indeed, they contain on average more than twice as much cobalt as the pentlandites from the Sudbury ore deposits. The analyzed pyrites were also unusually cobalt-rich.

TABLE 4. SUMMARY OF PENTLANDITE COMPOSITIONS

Atomic Percent	Fe	Ni	Co	S
Pentlandites Coexisting with Pyrite and Pyrrhotite				
Harris & Nickel (1972)	24.2	27.7	0.90	47.2
6 samples	(0.9)	(0.7)	(0.83)	(0.6)
Misra & Fleet (1973)	24.6	27.9	0.82	46.7
15 samples	(0.5)	(0.8)	(0.62)	(0.4)
Ramsden (1975)	24.2	28.1	0.50	47.2
37 samples	(0.8)	(1.0)	(0.14)	(0.6)
This Study	23.9	27.3	1.70	47.1
3 samples	(0.4)	(0.5)	(0.40)	(0.2)
Pentlandites from Sudbury Ores				
Hawley (1962)	24.9	27.0	0.64	47.5
12 samples	(0.8)	(0.5)	(0.03)	(1.3)

Numbers in parentheses are standard deviations.

Bulk chemical compositions calculated from modal analyses (Table 2) indicate that the magmatic sulfide grains contain up to 46 wt. % sulfur and up to 11 wt. % oxygen. Phase relations in the system Cu-Ni-Fe-S (Kullerud *et al.* 1969; Craig & Kullerud 1969) suggest that it is very unlikely that an iron-rich magmatic sulfide liquid would contain more than about 42 wt. % sulfur. To do so, the sulfide melt or its crystallization products would have to coexist with a nearly pure sulfur melt at some stage and this in turn would require unrealistically high S_2 and SO_2 fugacities (Naldrett & Gasparrini 1971). A consequence of this argument is that isochemical crystallization and cooling of a magmatic sulfide melt could produce a maximum of about 10% pyrite. Under the conditions of temperature and oxygen fugacity inferred below for the Main Irruptive magma, the maximum oxygen content of a sulfide melt would be about 5 wt. % on the basis of the experimental data for the system Fe-S-O (Naldrett 1969). Thus it is suggested that sulfur and oxygen have been added to many of the magmatic sulfide grains in the Main Irruptive samples during post-magmatic alteration. The persistent association of pyrite and magnetite noted above is significant in this regard. It will be noted (Table 2) that although the relative proportions of pyrrhotite and pyrite are extremely variable, the total amount of pyrrhotite+pyrite+magnetite is much less so. Thus it is suggested that the magnetite and most of the pyrite in the magmatic blebs were formed by secondary oxidation and sulfurization of primary pyrrhotite. The average pyrite:magnetite ratio is 6.4:1 in volume terms which corresponds to about 3.5:1 in molecular terms and suggests that the oxidation reaction has the following stoichiometry:

$$13\ FeS + 4\ O_2 + \tfrac{1}{2}\ S_2 = 2\ Fe_3O_4 + 7\ FeS_2 \quad (1)$$

As this reaction involves an 8.5% volume increase, the tiny grains of chalcopyrite and, less commonly, pyrrhotite which are disseminated in the silicate matrix of the magmatic blebs (e.g. Fig. 3B) may have been expelled from these blebs during alteration. The absence of primary magnetite from the blebs is consistent with the arguments of Naldrett (1969): he noted that although a sulfide melt which coexists with a silicate melt might contain a significant amount of oxygen, most of the oxygen could be lost to the silicate during crystallization of the sulfide if the oxygen and sulfur fugacities are buffered by the silicate. This condition is likely to be satisfied in a situation such as is envisaged here, that is, where small sulfide droplets are dispersed in a much larger volume of silicate matrix.

The orebodies localized in the marginal sublayer at Sudbury are typically mineralogically zoned with pn/cp ratios increasing from the outer contact to the inner contact with the Main Irruptive (e.g. Naldrett & Kullerud 1967; Souch *et al.* 1969). This zoning has been attributed to subsolidus diffusion in response to thermal gradients imposed across the orebodies during the cooling of the Main Irruptive (Naldrett & Kullerud 1967). Therefore, it may be assumed that there was very little compositional variation among or within the individual batches of molten sulfide which solidified to form the ores. Accordingly, the average po:cp:pn ratio of 70:15:15 reported by Hawley (1962) may be taken as a reflection of the initial bulk ore composition. Despite the rather large variation in the modal proportions of minerals in the magmatic grains from the Main Irruptive (Table 2), it is possible to make some general comparisons with the ore compositions. The Main Irruptive magmatic sulfides have distinctly higher proportions of po+py than do the ores. The pn/cp ratio in the Mafic Norite is approximately the same as that in the ores, whereas the ratios in the Quartz-rich and South Range Norites are significantly lower. Because nickel is concentrated in pentlandite and cobalt is concentrated in both pyrite and pentlandite, the modal and analytical data (Tables 2 & 3) indicate that the bulk compositions of the magmatic sulfides from the Main Irruptive have markedly higher Co/Ni ratios than those from the orebodies.

Experimental studies of the partitioning of metals among silicate minerals, silicate liquids and sulfide liquids (Duke, in press; Rajamani & Naldrett 1976; W. H. Maclean, oral presentation to Penrose Conference on Magmatic Sulfides 1975) indicate that the Cu/Ni, Co/Ni and Fe/(Cu+Ni+Co+Fe) ratios in a magmatic sulfide liquid will increase with the degree of differentiation of the silicate magma from which it exsolves. Thus it may be concluded that the Sudbury ore-melts separated from, or at least equilibrated with, a silicate magma which was slightly more mafic than the Mafic Norite but significantly less differentiated than the magmas from which the Quartz-rich and South Range Norites crystallized.

Deuteric or metamorphic sulfide grains

Sulfide grains which have clearly formed initially during either deuteric or metamorphic alteration of the Irruptive are typically discrete crystals or aggregates of crystals intergrown with secondary silicate minerals (Fig. 3D) or localized along microfractures in silicates or oxides (Fig. 4A). Pyrite is the most common phase to occur in these modes but examples with chalcopyrite, arsenopyrite and pyrrhotite have also been observed. It is possible that these secondary sulfide grains formed at the same time as the alteration of the primary magmatic grains described above. Thus the increase in sulfur and oxygen fugacities which caused the proposed reaction (1) to proceed to the right may also have promoted the breakdown and "sulfurization" of the primary silicates as well.

Supergene alteration

Most of the samples used in this investigation were collected from surface exposures and products of supergene alteration were common. The most frequently observed supergene effect is a complete coating of sulfide grains by hydrous iron oxide. Several sulfide species have also been produced by supergene alteration. Marcasite mantles pyrrhotite and lines fractures in it (Fig. 4B). Violarite was seen in a number of

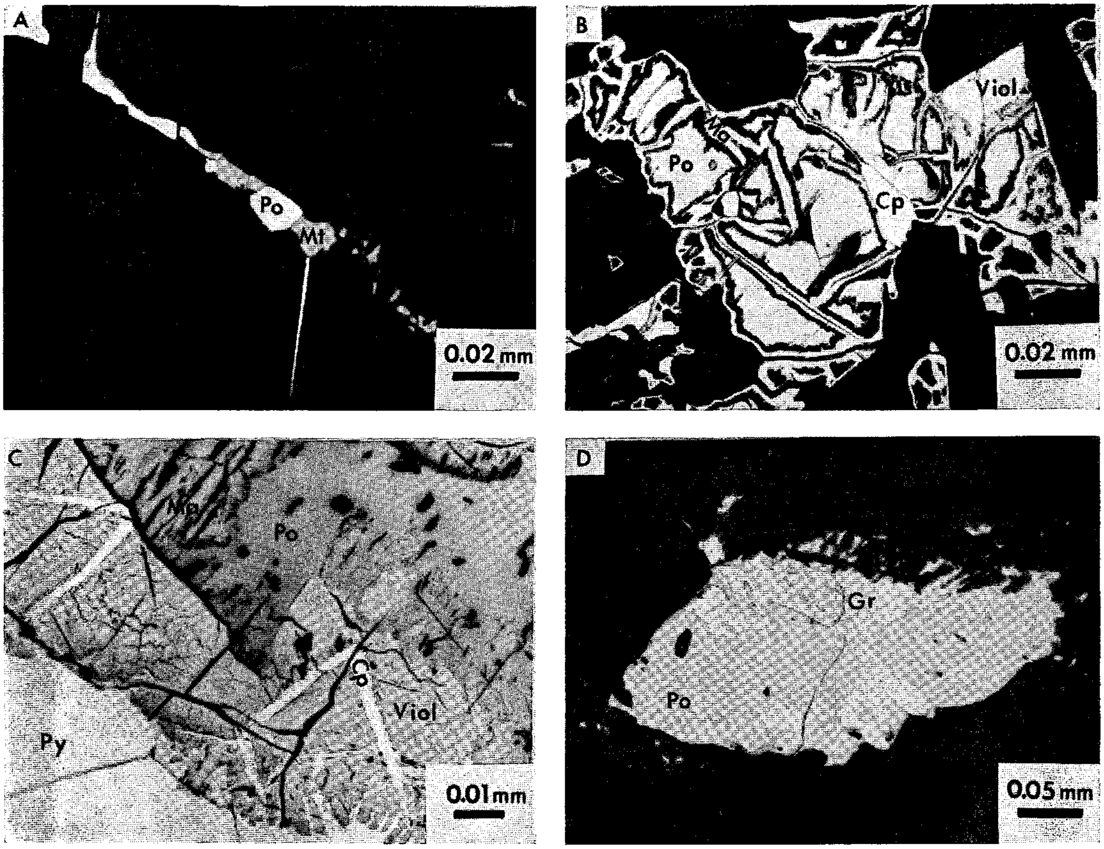

FIG. 4. (A) Deuteric or metamorphic sulfide texture. Pyrrhotite (Po) and magnetite (Mt) localized in a microfracture in biotite. Reflected light, oil immersion. (B) Marcasite (Ma) and violarite (Viol) occur as supergene alteration products of pyrrhotite and pentlandite respectively. Note the interstitial nature of the primary sulfide texture. Reflected light (C) Marcasite (Ma) and violarite (Viol) occur as supergene alteration products of pyrrhotite and pentlandite respectively. Note the fractured nature of the violarite and the veining of violarite by chalcopyrite (Cp). Reflected light, oil immersion. (D) Supergene alteration product of pyrrhotite, possibly griegite (Gr). Reflected light, oil immersion.

specimens but it is not possible to state conclusively whether it formed as an alteration of pyrrhotite or of pentlandite. Misra & Fleet (1974) noted that violarite which replaced pentlandite typically displays a granular habit whereas that which replaced pyrrhotite has a lamellar habit. Violarite observed in samples from the Main Irruptive always had a granular habit but did not occur with remnant pentlandite (Fig. 4C). The microprobe analyses of violarite (Table 3) are inferior in that the weight percentages of the elements sum to substantially less than 100%. Misra & Fleet (1974) encountered a similar problem which they attributed to the fractured and porous nature of supergene violarite. The same explanation may apply here (Fig. 4C) and it may be assumed that the relative proportions of the elements are nearly correct. The violarites are slightly sulfur-deficient with respect to stoichiometric $(Fe,Ni)_3S_4$ in that they contain from 55.1 to 55.7 at. % sulfur, whereas the stoichiometric value is 57.15. This apparent sulfur deficiency is a feature of supergene violarite which has been noted previously (Misra & Fleet 1974; Hudson & Groves 1974). These data support the observation by Misra & Fleet that the solid-solution range of natural violarite extends to much more iron-rich compositions than had been believed previously.

An unusual sulfide alteration product of pyrrhotite was observed in one sample (Fig. 4D). This material has a polishing hardness and reflectivity greater than those of pyrrhotite and forms as blades parallel to the basal plane in its pyrrhotite host. The blades are optically similar to griegite (Fe_3S_4) but have an apparent formula, $Fe_{2.7}Ni_{0.1}S_{4.0}$. The microprobe analysis of this phase (Table 3, No. 6 Gr) sums to only 95.3 wt. %, several replications giving nearly equivalent totals and atomic proportions of constituents. Wavelength scans did not reveal the presence of more than trace amounts of other elements.

SULFUR IN THE MAIN IRRUPTIVE

Concentration of sulfur in the rocks

Sulfur analyses of 55 samples collected at intervals of approximately 75 metres along the Blezard traverse on the south range were carried out using a LECO automatic titration system and the results are illustrated in Figure 5. The rocks of the south range have been metamorphosed and caution must be exercised when attempting to infer the primary (i.e. pre-metamorphic) concentrations of a volatile constituent such as sulfur. Indeed it was concluded above that post-magmatic processes have added sulfur to many of the rocks. Several samples plotted in Figure 5 contain anomalously high concentrations of sulfur and the sulfides in these samples are predominantly of the metamorphic or deuteric textural type. For example, the specimen illustrated in Figure 3D is from the sulfur-rich zone at the contact of the South Range Norite with the Upper Gabbro where deformation of the Irruptive has been relatively intense. However, the analytical data and the less frequent observation of magmatic sulfide textures in the higher levels of the Irruptive suggest that the primary concentration of sulfur decreased upwards from the base of the South Range Norite. Thus average sulfur concentration is 467 ppm in the Quartz-rich Norite, 628 ppm in the South Range Norite, 332 ppm in the Upper Gabbro, and 35 ppm in the Micropegmatite. In contrast, the Sublayer Norites, with which the ores are associated, are much richer in sulfur and average about 1800 ppm (South & Podolsky 1966).

Solubility of sulfur in the Irruptive magma

The textural evidence presented above indicates that droplets of an immiscible sulfide liquid separated from the magma which formed the lower part of the exposed Main Irruptive at an early stage of its crystallization and it is appropriate to ascertain whether the chemical data support this suggestion. The solubility of sulfur in the Sudbury norite magmas is not known explicitly, but may be estimated on the basis of experimental studies by Haughton *et al.* (1974). The maximum amount of sulfur that a mafic melt will dissolve is apparently directly proportional to temperature and the activity of ferrous iron but inversely proportional to the oxygen fugacity (although recent studies by Shima & Naldrett (1975) suggest that the relationship of solubility to oxygen fugacity is more

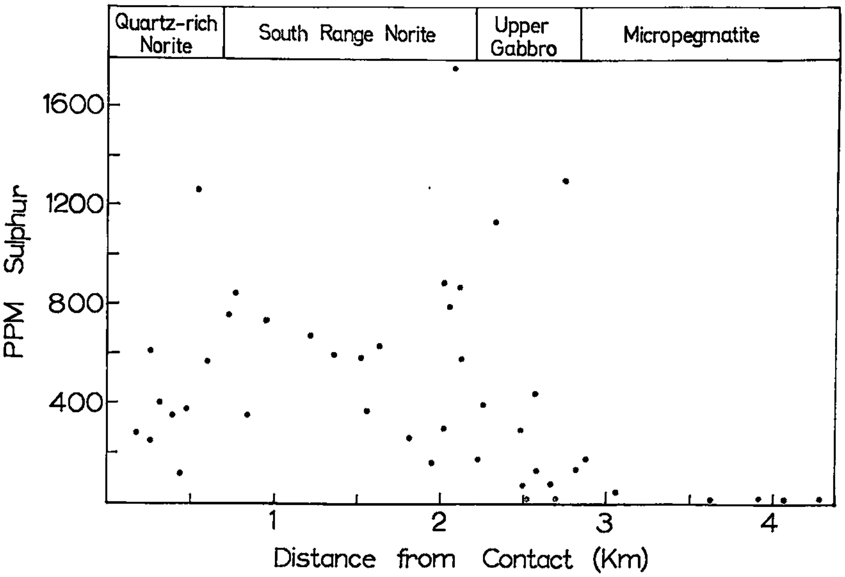

FIG. 5. Sulfur analyses of samples collected along the Blezard section (see Fig. 1). The abscissa gives the horizontal distance from the outer contact of the Main Irruptive

complex than a simple inverse variation). The activities of other magma constituents are important inasmuch as they influence the ferrous iron activity.

The fact that the Main Irruptive is a differentiated body, coupled with the absence of chilled margins, make it difficult to estimate the composition of the magma which formed the part of the Irruptive which was sampled. Moreover, the relative proportions of norite, granophyre, and transitional gabbro exposed at the surface are not representative of the intrusion as a whole if recent reconstructions are accepted (e.g. Naldrett *et al.* 1970). The overall proportion of granophyre and transitional gabbro is probably much smaller than indicated at surface. It was noted above that the Quartz-rich Norite is regarded as a marginal or border facies and its average composition will be taken as a first approximation of that of the Main Irruptive magma. The bulk rock analyses of Collins (1934) for samples which would be classified as Quartz-rich Norite under the present scheme have been averaged (Table 5).

TABLE 5. COMPOSITIONS OF QUARTZ-RICH NORITE AND SULFUR-SATURATED LIQUIDS FROM EXPERIMENTS OF HAUGHTON *et al.* (1974)

	Quartz-rich Norite*	Experiment 1F1**	Experiment 4F1**
SiO_2	54.27	53.92	52.54
TiO_2	0.90	2.12	2.12
Al_2O_3	18.01	20.06	16.20
Fe_2O_3	2.11	-	-
FeO	6.94	6.51	9.74
MnO	0.12	-	-
MgO	3.93	6.24	6.04
CaO	7.08	8.73	8.54
Na_2O	2.51	1.81	2.46
K_2O	1.19	0.88	1.13
S	0.047	0.048	0.071
T°C	1200	1200	1200
log fO_2	-9 ± 1	-10.2	-9.73

* Major-element concentrations from Collins (1934); sulfur concentration determined in present study.

**Experimental data from Haughton *et al.* (1974); iron reported as FeO.

The T and $f(O_2)$ of a magma of this composition may be estimated from published melting studies of similar rocks. The liquidus temperature under water pressures less than about 1 kbar is not likely to be higher than 1200°C. The ratio of $FeO{:}(FeO+Fe_2O_3)$ is 0.76 which indicates a magmatic oxygen fugacity of 10^{-9+1} at 1200°C (Fudali 1965; Hill & Roeder 1974). This probably represents a maximum value since the rocks have been oxidized somewhat since their crystallization. The compositional parameters from the experiments of Haughton *et al.* (1974) which most closely match those of the Quartz-rich Norite are included in Table 5. The FeO content of the norite is about midway between those of the experimental products and thus 600 ppm is a realistic estimate of the solubility of sulfur in the norite magma. Therefore, the average of 467 ppm S in the Quartz-rich Norite is lower, but of the same order of magnitude as the estimated solubility. Although the magma which differentiated to form the Main Irruptive may have been slightly undersaturated with respect to sulfur at the time of emplacement, it would have soon become saturated with the onset of cooling and crystallization. Settling of an early-formed immiscible sulfide melt may have led to the apparent enrichment of sulfur in the lower part of the main cumulative sequence (i.e., the base of the South Range Norite) and would account for the depletion of sulfur upwards in the Irruptive.

It is interesting to compare the concentration and estimated solubility of sulfur in the Main Irruptive magma to those of two layered intrusions which do not have associated sulfide ore deposits. Shirey (1975) has estimated that the initial magma of the Kiglapait intrusion contained about 280 ppm S, whereas he inferred that the saturation point would be about 2900 ppm. The chilled margin of the Skaergaard intrusion contains about 50 ppm S (Wager & Brown 1967) and this value may be taken as an approximation of the concentration in the initial magma. The sulfur solubility estimated by comparison with the experimental results of Haughton *et al.* (1974) would be 1100 ppm or greater. Thus it would seem that the initial magmas of both the Kiglapait and Skaergaard intrusions had sulfur concentrations which were at least an order of magnitude below the saturation point. These observations emphasize that in exploring for magmatic sulfide deposits in plutonic rocks, an effort should be made to identify intrusions which were saturated with sulfur at the time of emplacement. Evidence for sulfur saturation should be sought through investigations of both sulfur concentration and sulfide textures.

CONCLUSIONS

The textures of sulfide grains in the Mafic Norite, Quartz-rich Norite, and the lower two-thirds of the South Range Norite indicate that molten sulfide droplets were present at an early stage in the crystallization of the rocks. The concentration of sulfur in these rocks also suggests that the Main Irruptive magma was either saturated or just slightly undersaturated with sulfur when it was emplaced. There is no evidence of the presence of magmatic sulfide in the uppermost South Range Norite, the Upper Gabbro, the Felsic Norite, the Oxide-rich Gabbro, or the Micropegmatite. Mild sulfurization and oxidation during deuteric alteration or later metamorphism has led to the development of secondary pyrite in most rocks of the Main Irruptive.

Although we believe that the Main Irruptive magma may have been saturated with sulfur when emplaced, it is stressed that the evidence does not indicate that molten sulfides settled from the Main Irruptive magma *in situ* to form the orebodies. Rather, the lower proportion of iron sulfides and the lower cp/pn and Co/Ni ratios of the ores relative to the Main Irruptive magmatic sulfides indicate that the ores equilibrated with a less fractionated magma than that which formed the exposed part of the Main Irruptive.

ACKNOWLEDGMENTS

The electron microprobe analyses were carried out in the laboratory of Professor J. C. Rucklidge of the University of Toronto. Dr. V. Rajamani provided the standards for the microprobe analysis and Dr. O. P. Malik assisted in the operation of the instrument. Professor R. H. Hewins of Rutgers University supplied samples from the North mine. R. A. Alcock, E. F. Pattison, D. Phipps, C. Gourley, D. Mahaffy, A. Smeeth and D. Sly of the International Nickel Company were very helpful in arranging for samples to be collected at the Little Stobie mine and in providing samples for sulfur analysis. B. O'Donovan of the University of Toronto is thanked for his assistance with the photography. The first author was supported by a National Research Council Postdoctorate Fellowship and research expenses were defrayed by National Research Council Grant No. A4244 to the second author.

REFERENCES

BRAY, J. V. G. (1972): New developments in Sudbury geology. *Geol. Assoc. Can. Spec. Pap.* **10**.

CABRI, L. J. (1973): New data on phase relations in the Cu-Fe-S system. *Econ. Geol.* **68**, 443-454.

COLLINS, W. H. (1934): Life history of the Sudbury nickel irruptive (1). *Trans. Royal Soc. Can.*, Sect. IV, **28**, 123-178.

CRAIG, J. R. (1973): Pyrite–pentlandite and other low-temperature relations in the Fe-Ni-S system. *Amer. J. Sci.* **273-A**, 496-510.

———— & KULLERUD, G. (1969): Phase relations in the Cu-Fe-Ni-S system and their application to magmatic ore deposits. *In* Magmatic Ore Deposits (H. D. B. Wilson, ed.), *Econ. Geol. Monogr.* **4**, 344-358.

DUKE, J. M. (in press): Distribution of the period four transition elements among olivine, calcic clinopyroxene and mafic silicate liquid: experimental results. *J. Petrology*.

FUDALI, R. F. (1965): Oxygen fugacities in basaltic and andesitic magmas. *Geochim. Cosmochim. Acta* **29**, 1063-1075.

GASPARRINI, E. & NALDRETT, A. J. (1972): Magnetite and ilmenite in the Sudbury Nickel Irruptive. *Econ. Geol.* **67**, 605-621.

HARRIS, D. C. & NICKEL, E. H. (1972): Pentlandite compositions and associations in some mineral deposits. *Can. Mineral.* **11**, 861-878.

HAUGHTON, D. R., ROEDER, P. L. & SKINNER, B. J. (1974): Solubility of sulphur in mafic magmas. *Econ. Geol.* **69**, 451-467.

HAWLEY, J. E. (1962): The Sudbury ores, their mineralogy and origin. *Can. Mineral.* **7**, 1-207.

HEWINS, R. H. (1971): *The Petrology of Some Marginal Mafic Rocks Along the North Range of the Sudbury Irruptive*. Ph.D. thesis, Univ. Toronto.

———— (1974): Pyroxene crystallization trends and contrasting augite zoning in the Sudbury Nickel Irruptive. *Amer. Mineral.* **59**, 120-126.

HILL, R. E. & ROEDER, P. L. (1974): The crystallization of spinel from basaltic liquid as a function of oxygen fugacity. *J. Geol.* **82**, 709-730.

HUDSON, D. R. & GROVES, D. I. (1974): The composition of violarite coexisting with vaesite, pyrite, and millerite. *Econ. Geol.* **69**, 1335-1340.

IRVINE, T. N. (1975): Crystallization sequences in the Muskox intrusion and other layered intrusions — II. Origin of chroitite layers and similar deposits of other magmatic ores. *Geochim. Cosmochim. Acta* **39**, 991-1020.

KISSIN, S. A. (1974): *Phase Relations in a Portion of the Fe-S System*. Ph.D. thesis, Univ. Toronto.

KULLERUD, G., YUND, R. A. & MOH G. H. (1969): Phase relations in the Cu-Fe-S, Cu-Ni-S and Fe-Ni-S system. *In* Magmatic Ore Deposits (H. D. B. Wilson, ed.), *Econ. Geol. Monogr.* **4**, 323-343.

MISRA, K. C. & FLEET, M. E. (1974): Chemical composition and stability of violarite. *Econ. Geol.* **69**, 391-403.

NALDRETT, A. J. (1969): A portion of the system Fe-S-O between 900° and 1080°C and its application to sulphide ore magmas. *J. Petrology* **10**, 171-201.

———— & KULLERUD, G. (1967): A study of the Strathcona Mine and its bearing on the origin of the nickel-copper ores of the Sudbury district, Ontario. *J. Petrology* 8, 453-531.

————, BRAY, J. G., GASPARRINI, E., PODOLSKY, T. & RUCKLIDGE, J. C. (1970): Cryptic variation and petrology of the Sudbury Nickel Irruptive. *Econ. Geol.* **65**, 122-155.

————, HEWINS, R. H. & GREENMAN, L. (1972): The Main Irruptive and the sub-layer at Sudbury, Ontario. *Proc. 24th Int. Geol. Cong.* **4**, 206-213.

PEREDERY, W. V. & NALDRETT, A. J. (1975): Petrology of the upper Irruptive rocks, Sudbury, Ontario. *Econ. Geol.* **70**, 164-175.

RAE, D. R. (1975): *Inclusions in the Sublayer from Strathcona Mine, Sudbury, and Their Significance.* M.Sc. thesis, Univ. Toronto.

RAJAMANI, V. & NALDRETT, A. J. (1976): Partitioning of Fe, Ni, Cu and Co between sulfide and silicate liquids. *Geol. Assoc. Can. — Mineral. Assoc. Can. Program Abstr.* 1, 56.

RAMSDEN, A. R. (1975): Compositions of co-existing pyrrhotites, pentlandites and pyrites at Spargoville, Western Australia. *Can. Mineral.* **13**, 133-137.

SHIMA, H. & NALDRETT A. J. (1975): Solubility of sulfur in an ultramafic melt and the relevance of the system Fe-S-O. *Econ. Geol.* **70**, 960-967.

SHIREY, S. B. (1975): Sulfides and sulfur content of the Kiglapait layered intrusion, Labrador. *Geol. Amer. Program Abstr.* 7, 858.

SOUCH, B. E., PODOLSKY, T. & GEOLOGICAL STAFF (1969): The sulphide ores of Sudbury: their particular relation to a distinctive inclusion-bearing facies of the Nickel Irruptive. *In* Magmatic Ore Deposits (H. D. B. Wilson, ed.), *Econ. Geol. Monogr.* 4, 252-261.

WAGER, L. R. & BROWN, G. M. (1967): *Layered Igneous Rocks.* Freeman & Co., San Francisco.

YUND, R. A. & KULLERUD, G. (1966): Thermal stability of assemblages in the Cu-Fe-S system. *J. Petrology* 7, 454-488.

Received February 1976, emended May 1976.