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GENESIS OF Cu–Ni SULFIDE MINERALIZATION IN THE SOUTH KAWISHIWI INTRUSION, SPRUCE ROAD AREA, DULUTH COMPLEX, MINNESOTA

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ABSTRACT

The South Kawishiwi intrusion is one of several within the Duluth Complex, Minnesota, the principal exposed plutonic component of the 1.1 Ga Midcontinent Rift system. In the Spruce Road area, the South Kawishiwi intrusion is divisible into seven distinct troctolitic to gabbroic units, four of which contain 1 to 5 vol.% of disseminated pyrrhotite, cubanite, chalcopyrite, and pentlandite. Values of $\delta^{34}S$ in the mineralized units range from 3.8 to 10.2‰, and are distinctly different from those of non-mineralized rocks, which range from –3.4 to 2.8‰. The proposed model for the genesis of the sulfides involves the mixing of sulfur derived from two sources, accumulation of immiscible sulfide liquid, and emplacement of sulfide-saturated magmas. The relatively evolved, high-Al olivine tholeiite parental magmas of the intrusive sequence most likely resulted from fractional crystallization of a mantle-derived primary melt in a chamber in the lower crust or upper mantle. During this process, sulfide saturation would have been achieved, with chalcophile elements removed from the magma into a coexisting sulfide liquid. Emplacement of the sulfide-saturated melt into a higher-level staging chamber permitted the assimilation of sulfur from metasedimentary country-rocks. Reaction between externally derived sulfur and metals initially present in the melt as silicate, oxide, or neutral species would have produced a second generation of immiscible sulfide liquid that mixed with that of mantle origin. Sulfide-rich rocks of the South Kawishiwi intrusion represent melts derived from the high-level chamber that had experienced contamination with sulfur of crustal origin. Because of the wide range in possible contaminant $\delta^{34}S$ values (*e.g.*, 0 to 29‰ in sulfides from metasedimentary country-rocks), it is difficult to accurately assess the proportion of country-rock sulfur present in the mineralized units, but a range of from 30 to 70% is consistent with available data. Sulfide assemblages are mineralogically zoned, such that pyrrhotite-rich layers are overlain by (cubanite + chalcopyrite)-rich layers. *In situ* crystallization, controlled by boundary-layer fractionation and upward expulsion of Cu- and Ni-enriched residual liquid, is proposed to explain the zonation. Upward increases in contents of Cu and Ni, as well as of incompatible elements such as Zr, Y, and P, may be controlled by a filter-pressing mechanism, or may result from the decrease in density of an interstitial liquid related to enrichment of volatiles.

Keywords: disseminated Cu–Ni mineralization, anomalous $\delta^{34}S$ values, sulfide mineral zoning, South Kawishiwi intrusion, Duluth Complex, Minnesota.

SOMMAIRE

Le massif intrusif de South Kawishiwi fait partie du complexe intrusif de Duluth, au Minnesota, l'expression plutonique la plus importante des suites liées au rift médiocontinental, et mis en place il y a 1.1 milliard d'années. Dans la région de Spruce Road, le massif de South Kawishiwi comporte sept unités troctolitiques et gabbroïques distinctes, dont quatre contiennent de 1 à 5% (par volume) de pyrrhotite, cubanite, chalcopyrite et pentlandite disséminées. Les valeurs de $\delta^{34}S$ dans ces unités minéralisées vont de 3.8 à 10.2‰, et se distinguent donc de celles des roches non minéralisées, dans l'intervalle –3.4 à 2.8‰. Le modèle que nous proposons requiert un mélange de soufre dérivé de deux sources, une accumulation de liquide sulfuré, et la mise en place de magmas saturés en soufre. Les magmas qui sont responsables de la suite plutonique, de nature tholéiitique à olivine et enrichis en Al, seraient probablement dus à la cristallisation fractionnée d'un magma primaire issu du manteau et résidant dans une chambre dans la croûte inférieure ou dans le manteau. Au cours de ce processus, une saturation en soufre aurait eu lieu, et les éléments à tendance chalcophile auraient été captés par le liquide sulfuré. La mise en place de ce liquide basique saturé en sulfure dans une chambre plus près de la surface aurait permis l'assimilation de soufre des roches encaissantes métasédimentaires. Une réaction entre le soufre à dérivation externe et les métaux présents au départ sous forme de silicates, d'oxydes, ou d'espèces neutres dans le magma, aurait produit une seconde génération de liquide sulfuré immiscible qui se serait mélangée à l'autre, d'origine mantellique. Les roches enrichies en sulfures dans le massif de South Kawishiwi sont le produit de

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cristallisation de magmas dérivés de la chambre supérieure qui ont été contaminés avec du soufre d'origine crustale. A cause du grand intervalle des valeurs de $\delta^{34}S$ dans les sulfures des roches métasédimentaires responsables de la contamination (*e.g.*, de 0 à 29‰), il est difficile d'évaluer avec justesse la proportion des roches encaissantes présentes dans les unités minéralisées; une proportion entre 30 et 70% concorderait avec les données disponibles. Les assemblages de sulfures sont zonés, de telle sorte que les assemblages à pyrrhotite sont recouverts par des niveaux riches en cubanite + chalcopyrite. Une cristallisation *in situ*, régie par le fractionnement d'un liquide dans la couche enrichie en éléments rejetés par les cristaux, et par l'expulsion vers le haut d'un liquide résiduel enrichi en Cu et en Ni, pourrait expliquer la zonation observée. Les augmentations vers le haut des teneurs en Cu et en Ni, et de façon parallèle, des teneurs en Zr, Y et P, pourraient résulter d'une séparation forcée du liquide sous pression, ou peut-être d'une diminution de la densité d'un liquide interstitiel à cause d'un enrichissement en phase volatile.

(Traduit par la Rédaction)

Mots-clés: minéralisation disséminée à Cu–Ni, valeurs $\delta^{34}S$ anomales, zonation en minéraux sulfurés, massif intrusif de South Kawishiwi, complexe de Duluth, Minnesota.

INTRODUCTION

Sulfide mineralization in the Duluth Complex of Minnesota (Fig. 1) constitutes a major Cu–Ni resource, with estimated reserves of over six billion tonnes grading 0.66 wt.% Cu and 0.17 wt.% Ni (Listerud & Meineke 1977). Localized enrichment of the platinum-group elements (PGE) has been reported (*e.g.*, Sabelin *et al.* 1986, Ripley 1990, Severson & Barnes 1991, Severson 1994). Naldrett (1992) has suggested that the Duluth Complex and associated plutonic rocks related to the Midcontinent Rift System are prime targets of exploration for Noril'sk-type Cu–PGE ores.

Sulfide mineralization is located primarily along the western margin of the Complex, where troctolitic and gabbroic rocks are in contact with country rocks, including metasedimentary rocks of the Lower Proterozoic Animikie Group and Archean rocks of the Giants Range Batholith (Figs. 1, 2). Two composite intrusions, the South Kawishiwi intrusion to the north and the Partridge River intrusion to the south (Fig. 2), are host to most of the mineralization. The sulfide mineralization is generally disseminated; massive sulfides are rarely developed. Several studies have focused on the genesis of the Cu–Ni mineralization in the Partridge River intrusion, and the possible importance of interaction between mafic magma and sulfide-bearing, pelitic country-rocks (*e.g.*, Ripley 1981, Tyson & Chang 1984, Pasteris 1984, Ripley & Alawi 1986, Ripley 1990, Geerts *et al.* 1990, Severson 1991). In addition, geochemical studies by Grant & Molling (1981), Ripley & Al-Jassar (1987), Ripley & Taib (1989), Chalokwu & Grant (1990), Grant & Chalokwu (1992), and Chalokwu *et al.* (1993) have dealt with the

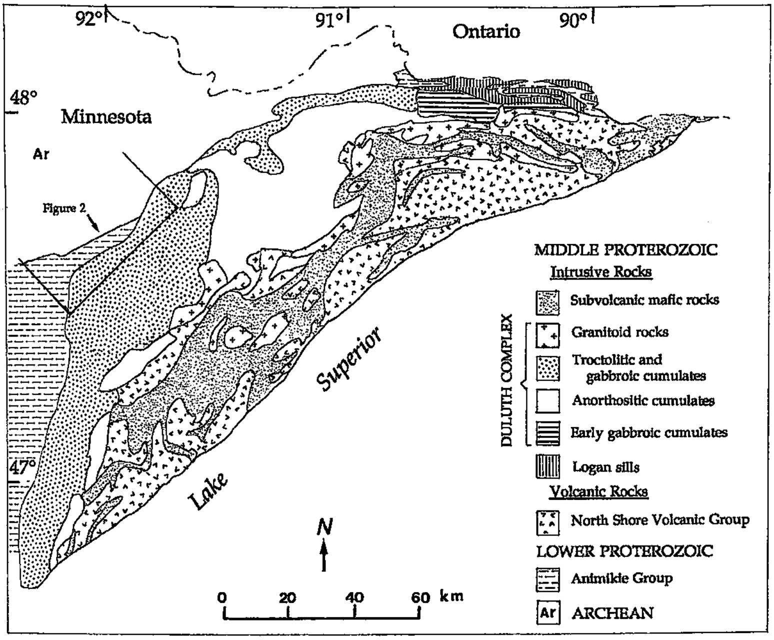

FIG. 1. Generalized geological map of northeastern Minnesota (modified from Miller & Weiblen 1990), showing location of the Duluth Complex.

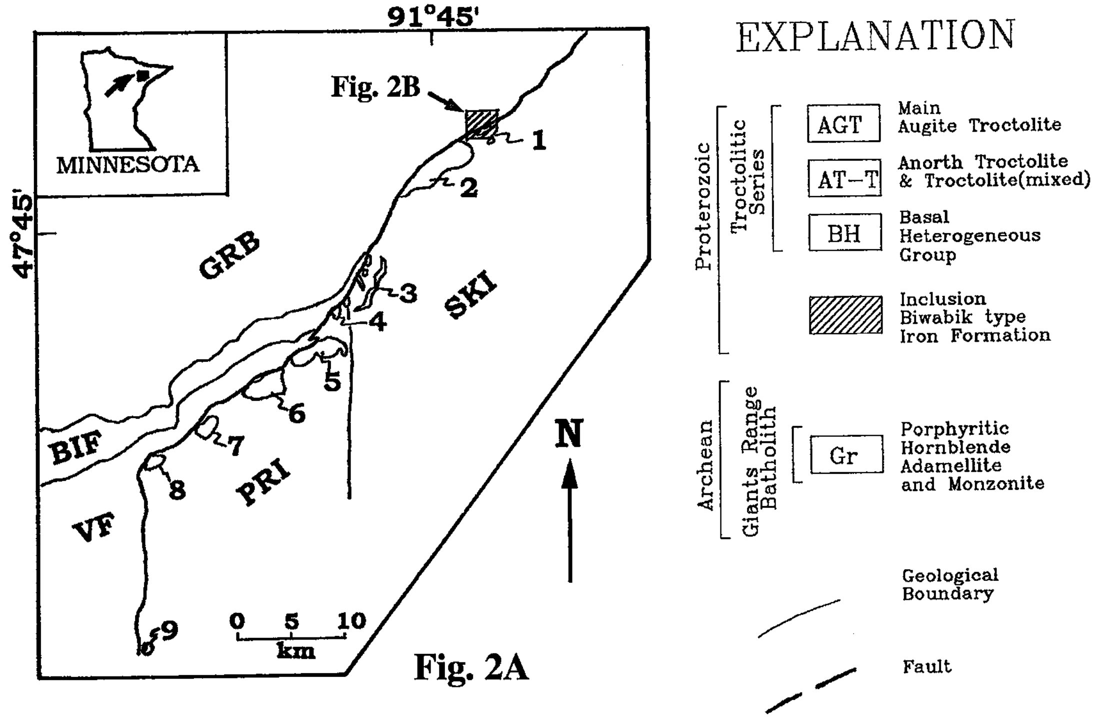

Fig. 2A

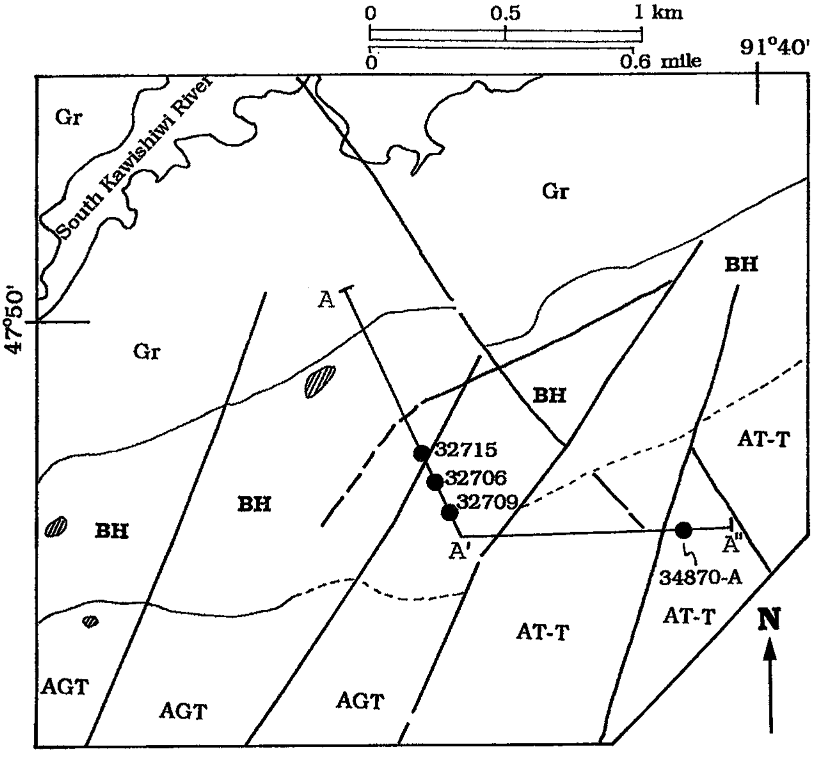

Fig. 2B

FIG. 2. A) Generalized geological map of the western margin of the Duluth Complex showing the Partridge River and South Kawishiwi intrusions (modified from Severson 1991). Locations of principal Cu–Ni prospects: 1 Spruce Road, 2 Maturi, 3 Dunka Pit, 4 Serpentine, 5 Babbitt, 6 Dunka Road, 7 Wetlegs, 8 Wyman Creek, 9 Water Hen. B) Geological map of the Spruce Road area, modified from Severson (1994). Locations of drill cores examined in this study are shown as solid dots.

petrogenesis of the Partridge River intrusion. Mineralization associated with the South Kawishiwi intrusion is similar in form to that in the Partridge River intrusion, but the country rocks are primarily sulfide-poor granitic rocks of the Giants Range Batholith (Fig. 2). Reconnaissance studies of the association between rock types and sulfide mineralization in various portions of the South Kawishiwi intrusion have been conducted by Weiblen & Morey (1976), Bonnichsen *et al.* (1980), and Foose & Weiblen (1986). Studies of PGE mineralization in the South Kawishiwi intrusion have been undertaken by Sabelin *et al.* (1986), Kuhns *et al.* (1990), and Severson (1994).

The Partridge River intrusion was emplaced into sulfide-bearing pelitic metasedimentary rocks of the Virginia Formation and Biwabik Iron Formation. Most researchers agree that the assimilation of sulfur from the metasedimentary sequences was a key process for ore genesis (*e.g.*, Ripley 1981, Ripley & Al-Jassar 1987), but questions remain concerning the timing of the addition of external sulfur, and to the relative proportions of externally derived and magmatic sulfur. At the Spruce Road deposit (Fig. 2), felsic to intermediate plutonic rocks of Archean age are found at the basal contact of the mafic intrusions. These rocks are locally sulfide-bearing (see below), but in general contain much less sulfur than the metasedimentary rocks of the Virginia Formation. A study of the Spruce Road deposit was initiated to evaluate possible differences between specific occurrences of sulfide mineralization in the Complex in relation to differences in both the country-rock lithology and the stratigraphy of the host intrusion.

REGIONAL STRATIGRAPHY OF THE SOUTH KAWISHIWI TROCTOLITE SERIES AND GEOLOGY OF THE SPRUCE ROAD AREA

Most of the troctolitic units within the Duluth Complex are sheet-like to saucer-shaped. However, the lack of abundant outcrop exposure and critical drill-core information has hampered the precise determination of intrusive contacts and of the lateral continuity of individual units. Severson (1994) has identified an internally consistent stratigraphic sequence in the eastern Babbitt – Spruce Road area that is referred to as the South Kawishiwi Troctolite Series. On the basis of features observed in drill core from Wetlegs to Babbitt (Fig. 2), it is evident that the South Kawishiwi Troctolite Series is petrologically different from the troctolite series defined by Severson & Hauck (1990) for the Partridge River intrusion. Severson (1994) has defined seventeen distinct units on the basis of macroscopic variations in mineralogy and texture, although not all are present in all localities of the South Kawishiwi intrusion. A brief description of Severson's (1994) units is given in Table 1. Several of these units have also been described by Bonnichsen (1972), Foose (1984) and Foose & Weiblen (1986), although widespread correlation was not attempted. Rock types include norite, gabbro, several varieties of troctolite, peridotite, and dunite. Precise correlation of units in the South Kawishiwi sequence is very difficult owing in part to lateral changes in rock type, and in part to dislocations due to faulting. The rift-zone environment has fostered the development of a complicated stratigraphy of igneous units, characterized by multiple intrusions and probable replenishment of magma chambers. Deciphering the temporal and chemical relationships among major units and subunits in sequences such as the Partridge River and South Kawishiwi Troctolite Series remains as a major task in unraveling the evolution of the Duluth Complex and its role in rift-related magmatism. It should be noted that the stratigraphic framework of Severson & Hauck (1990) and Severson (1991, 1994) differs from that proposed by Martineau (1989), who defined at least six distinct intrusive bodies in the Wyman Creek – Spruce Road area. Martineau's overall division of the Complex into at least 40 distinct major intrusions illustrates the interpretive complexity associated with intrusive emplacement in a dynamic rift environment. It is likely that each intrusive body formed from several influxes of magma. Some of these influxes occurred late in the crystallization history of a particular intrusion and formed recognizable intrusive bodies. The work of both Martineau (1989) and Severson (1994) suggests that the South Kawishiwi intrusion comprises the crystalline products of several distinct influxes of magma.

Initial exploration of the Spruce Road deposit (Fig. 2) was conducted by the International Nickel Company (now INCO Ltd.) in 1987. The company drilled approximately 175 drill holes. Unfortunately, most of the core was rendered unusable by a fire. Outcrops are rare in the Spruce Road area, and most of the geological information regarding the deposit was derived from company records and recent study of the remaining drill core (Severson 1994).

Although footwall rocks are part of the Giant's Range Batholith, inclusions of rocks of the Animikie Group, Virginia Formation, Biwabik Iron Formation (Fig. 1) and Keewenaawan basalt are found in the South Kawishiwi intrusion. The presence of metasedimentary inclusions indicates that some of the parent magmas were intruded into metasedimentary sequences that represent a likely source for externally derived sulfur (see below). The term "Spruce Breccia" (*e.g.*, Wager *et al.* 1969) was applied to rocks that either contain a large number of metasedimentary inclusions or numerous textural varieties of troctolite. According to Severson's (1994) classification, the Spruce Breccia is part of the Basal Heterogeneous zone, in which textural and mineralogical variations are common over small spatial intervals. Whether the textural varieties are the result of earlier intrusive rocks

TABLE 1. SUMMARY OF THE KEY CHARACTERISTICS OF UNITS IN THE SOUTH KAWISHIWI TROCTOLITE SERIES[1]

	Unit	Description
Top	Anorthositic Troctolite	Homogeneous - textured with High Picrite #1 at its base; > 366m.
	Anorthositic Troctolite and Troctolite	Interlayered rock types, gradational contact with underlying Main Augite Troctolite; 366 - 610m.
	Updip Wedge	Present only locally. Sulfide-bearing troctolite, plagioclase-rich troctolite and augite troctolite. Heterogeneous-textured. Two ultramafic subunits are present within thick sections; 31 - 274m.
	Main Augite Troctolite	Homogeneous with coarse, ophitic cpx and composite ilmenite-magnetite grains; 83 - 421m.
	Ultramafic One	Picrite and peridotite with interlayered homogeneous troctolite. Sulfide-bearing; 1.5 - 131m.
	Basal Heterogeneous Zone	Heterogeneous- and homogeneous-textured troctolite and lesser anorthositic troctolite. Sharp to gradational contacts. Sulfide-bearing; 27 - 518m.
	Anorthositic Troctolite to Troctolite	Homogeneous, sulfide-barren. Present above the Pegmatic unit; 21 - 366m.
	Ultramafic Two	Picrite, peridotite, olivine-rich troctolite alternate with troctolite. Massive oxide layers are absent. Sulfide-bearing only when contained in the Basal Heterogeneous Unit; 1.5 - 130m.
	Pegmatitic Unit of Foose (1984)	Pegmatitic troctolite to plagioclase-rich troctolite minor augite troctolite and olivine gabbro. Consistently above the Ultramafic Three Unit. Locally sulfide-bearing; 3 - 79m.
	Ultramafic Three	Picrite, peridotite, olivine-rich troctolite alternate with troctolite. Massive oxide layers occur up to ~15m thick. All rocks are sulfide-bearing; 1 - 125m.
Bottom	Augite Troctolite/Norite	Heterogeneous-textured. Norite more common at the base and augite troctolite in the upper portion. Sulfide-bearing, locally massive. Maximum Cu values up to 1.6 wt.%; 3 - 116m.

[1] After Severson, 1994.

Measurements in meters refer to the observed true thickness of the units.

being included in later magma, or the result of perturbations during magma crystallization, is not clear for all locations.

Rock types present in the southeastern portion of the Spruce Road area differ sharply from those present to the northwest (Fig. 2). Figure 3 is a cross section showing the relative position and attitude of drill cores examined during this study. Most of the rock types present in the northwestern sector correlate with Severson's (1994) Basal Heterogeneous group, many of which were referred to as Spruce Breccia by company geologists. Drill core 34870–A (Fig. 2), upon which this study is primarily based, transected many rock types not present to the northwest. A fault is inferred between the drill locations to explain the observed differences in the stratigraphy. Foose & Cooper (1981) and Severson (1994) described several faults in this area of the complex; most of these trend in a N–NE direction, and show little evidence of lateral motion. However, because some of the faults produce significant downdip dislocations, correlation of rock types across the faults is difficult.

SAMPLING AND ANALYTICAL METHODS

Samples for this project were taken from drill core provided by the American Copper and Nickel Company, Denver, Colorado (a subsidiary of INCO

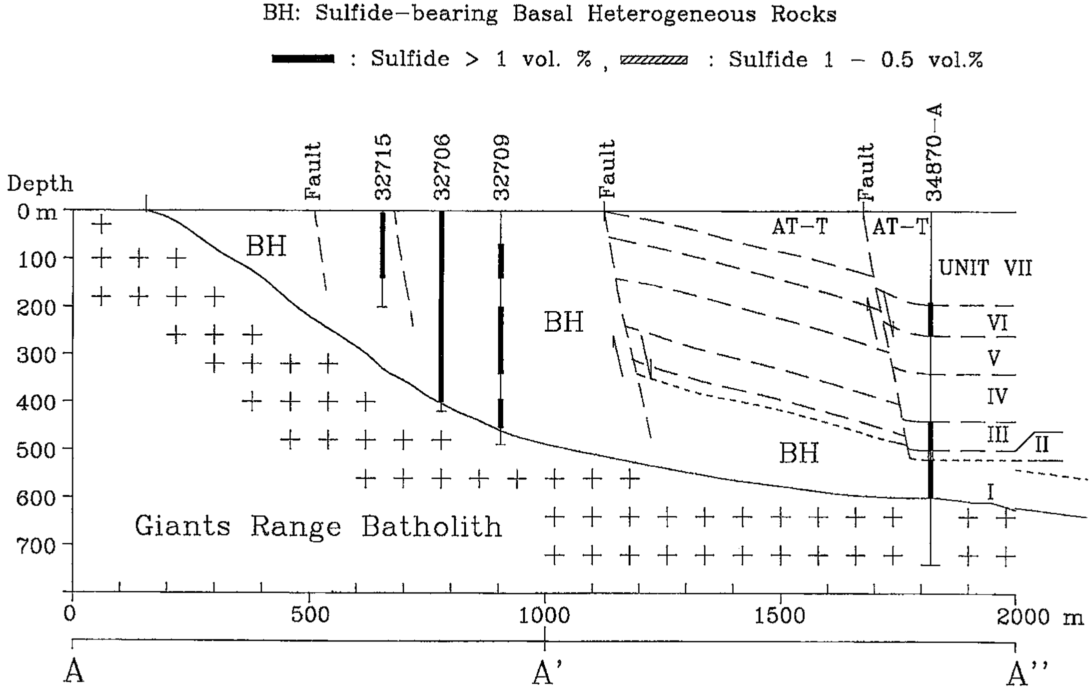

FIG. 3. Cross section along lines A–A′ and A′–AA″ of Figure 3. Rock types are those of Severson (1994). BH: basal heterogeneous zone, AT–T: anorthositic troctolite and troctolite. Units I – VII have been defined by Lee & Ripley (in press).

Ltd.), and by the Minnesota Department of Natural Resources, Hibbing, Minnesota (core 34870–A). The entire 740 m length of core 34870–A was sampled, but only the upper 213 m of cores 32706, 32709, and 32715 were available for collection. One hundred polished thin sections were examined using transmitted and reflected light microscopy. Modal analyses were obtained for 75 sections by counting a minimum of 2,500 points per section.

The concentration of major, minor, and trace elements for 65 whole-rock samples was obtained by X-ray fluorescence spectrometry (X-RAY Assay Laboratories, Don Mills, Ontario). Analyses were performed with a Philips 1600 spectrometer using glass disks. Detection limits are 0.01% and 10 ppm for major and trace elements, respectively. Concentrations of copper, Ni, and Y were determined for these samples using inductively coupled plasma – mass spectrometry at Indiana University. Analytical precision for major elements was better than 1% relative standard deviation, and 5% for trace elements. Total concentrations of sulfur and carbon were measured for 45 whole-rock powders using a LECO C/S 244 instrument at Indiana University. Multiple analyses of standards gave absolute standard deviations of ±0.02% for C and ±0.07% for S. More precise determinations of sulfur content were made at the time sulfur isotopic analyses were performed on low-sulfur samples. Samples were combusted *in vacuo*, and SO_2 was measured manometrically.

A total of 45 sulfur isotope measurements were made on whole-rock samples and mineral separates from drill core 34870–A. For sulfur isotope analyses, sulfide minerals were prepared by combustion with CuO in vacuum (Fritz *et al.* 1974). Liberated SO_2 gas was analyzed using a 6″, 60° sector Nuclide stable isotope ratio mass spectrometer at Indiana University. Results are reported in standard δ notation relative to Cañon Diablo Troilite, with an analytical precision of ±0.1‰.

SUMMARY OF UNITS PRESENT IN DRILL CORE 34870–A

Lee & Ripley (in press) have divided drill core 34870–A (Fig. 3) into seven units based on mineralogical and textural variations, as well as whole-rock and mineral-chemical variations. These units can be placed in the regional framework of the South Kawishiwi Troctolite Series defined by Severson (1994). Rock names are based on the scheme proposed by Miller & Weiblen (1990), and follow the conventional nomenclature sanctioned by the IUGS. Primocryst minerals are olivine and plagioclase, and in the terminology of cumulates (*e.g.*, Jackson 1967), the rocks are olivine–plagioclase and, more rarely, plagioclase cumulates. Rock types identified in drill core 34870–A include troctolite, melatroctolite, norite, olivine gabbro, gabbronorite, olivine oxide gabbro, gabbro, and olivine to orthopyroxene anorthosite (Fig. 4).

The footwall rocks are quartz monzonite to granodiorite of the Giants Range Batholith. The predominant mineral assemblage consists of plagioclase, K-feldspar, and lesser quartz, hornblende, biotite, magnetite, and apatite. K-feldspar decreases in abundance away from the contact with the South Kawishiwi intrusion. Chlorite and actinolite alteration of plagioclase and mafic minerals is most pronounced in close proximity to this contact. Clots of chlorite and actinolite (0.9 to

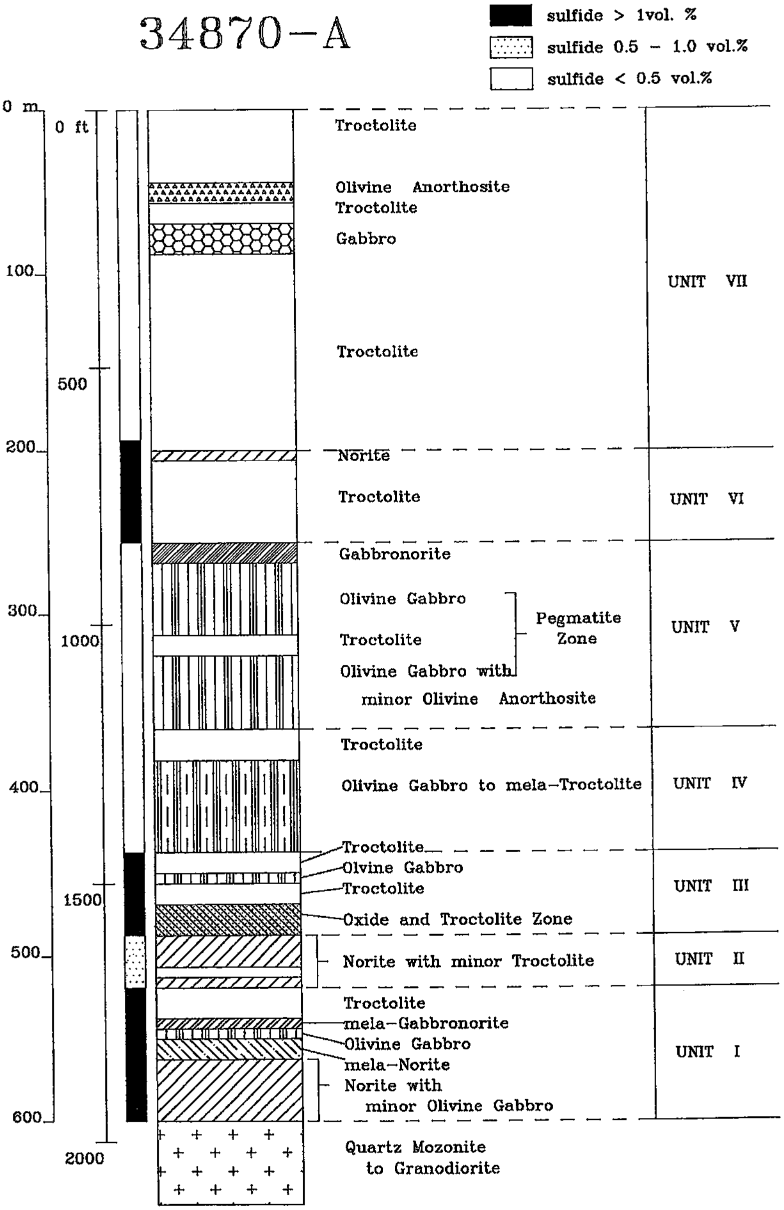

FIG. 4. Summary of stratigraphic variations within drill core 34870–A, South Kawishiwi intrusion, Spruce Road area.

2.9 mm across) are commonly associated with fine-grained sulfides similar in composition to those in the overlying intrusion (*e.g.*, pyrrhotite, cubanite, chalcopyrite, and pentlandite). These sulfide occurrences are restricted to within 40 m of the intrusive contact. Below this depth, the sulfur content in the Giants Range Batholith is very low (<0.04 wt.%), and the assemblage of primary sulfides consists of finely disseminated pyrite and minor chalcopyrite.

At Spruce Road, Unit I of the South Kawishiwi Troctolite Series comprises heterogeneous gabbroic and lesser troctolitic cumulates. Unit II is characterized by a lower content of olivine, and increased amounts of orthopyroxene and inverted pigeonite relative to Unit I. Chemical and isotopic data (see below) indicate that Unit II has experienced more crustal contamination than other units. Units I and II in core 34070-A are equivalent to Severson's (1994) Bottom Augite Troctolite–Norite and Basal Heterogeneous units (Table 1). Unit III consists of melatroctolite, troctolite and olivine gabbro, with local magnetite-rich layers. This unit correlates with Severson's (1994) U3 ultramafic horizon. Units I to III are sulfide-bearing (1 to 15 vol.% sulfides), and enriched in Fe, Mn and, locally, Ti. Unit IV consists of two cyclic units, each composed of an olivine-rich troctolite layer overlain by olivine gabbro and troctolite. Thin layers (~2–3 m) of olivine-poor rock types locally occur within the basal melatroctolite. Unit IV is enriched in Fe, Mn, and Mg, which reflects the great abundance of olivine-rich rock types. Unit V is characterized by an increase in plagioclase abundance, with evidence of differentiation culminating in the formation of pegmatitic layers. This unit is included in Severson's (1994) Basal Heterogeneous unit. Unit VI is a strongly altered, predominantly troctolitic sequence with up to 5 vol.% disseminated sulfide. Remnant olivine in this unit is strongly depleted in Ni relative to olivine in all other units, with concentrations as low as 200 ppm. Major- and trace-element contents of Unit VI are similar to those of Units III and IV, and it seems that Unit VI correlates with Severson's (1994) U1 ultramafic horizon. Unit VII is similar petrologically to Unit V, and primarily contains troctolite and olivine anorthosite, which form at least two cyclic units. Unit VII correlates with Severson's (1994) homogeneous Anorthositic Troctolite and Troctolite.

Evidence of alteration is present in all rocks of the South Kawishiwi intrusion in the Spruce Road area. Alteration, particularly intense within Unit VI, led to the serpentinization of olivine, conversion of plagioclase to chlorite, albite, epidote, calcite, prehnite, and amphibole, and the formation of chlorite and amphiboles from pyroxene, olivine, and biotite. In most samples, biotite is the principal hydrous mineral considered to have crystallized from interstitial melt. In all but five samples, the water structurally bound in magmatic biotite is less than 25% of the whole-rock water content, which indicates that the majority of the water is contained within secondary minerals.

DISTRIBUTION OF SULFIDE MINERALS

At Spruce Road, disseminated mineralization is concentrated in two specific parts of the stratigraphy, within Units I to III and Unit VI. The modal abundance of sulfides in these units varies from 0.5 to 15 volume % (Fig. 5). Although the host rocks vary significantly, the mineralogy and texture of the sulfide minerals are similar. Fine- to medium-grained sulfides occur interstitially to primocryst minerals. Principal sulfide minerals are pyrrhotite, cubanite, chalcopyrite, and pentlandite, accompanied by minor amounts of mackinawite, bornite, digenite, and sphalerite.

Zoning of the sulfide mineralization is an important feature. All of the mineralized units contain a basal zone enriched in pyrrhotite (70–100%) that is overlain by a zone enriched in cubanite and chalcopyrite (70–100%). Cubanite may occur as exsolution lamellae in chalcopyrite, or as individual grains associated with pyrrhotite. Within Units I–III, the proportion of cubanite exceeds that of chalcopyrite. In rocks with less than 0.5 volume % sulfide, chalcopyrite is the predominant sulfide mineral present, and commonly contains exsolved bornite. Within Units I–III, intergrowths of chalcopyrite and bornite occur exclusively as fine (typically <30 μm) grains around the margins of larger cubanite–pyrrhotite grains (Fig. 6). Similar distributions of chalcopyrite and cubanite have been reported for other areas in the complex by several investigators (*e.g.*, Ripley & Alawi 1986, Severson 1991, 1994, Sassani 1992). The modal abundance of pentlandite in rocks of the Spruce Road area never exceeds 20%. It is normally found as granular grains in pyrrhotite or cubanite, or as exsolution flames in pyrrhotite. Although the sulfide-bearing zone in Unit VI resides within highly altered rocks (chlorite, serpentine, actinolite, albite), the alteration is not restricted to the mineralized interval, but includes the basal portion of Unit VII and the top of Unit V. Sulfide zoning is the same as that observed in the basal units.

SULFUR ISOTOPIC STUDIES

Results of sulfur isotopic analyses are given in Table 2 and Figure 7. Sulfide minerals in Units I–III and VI show elevated $\delta^{34}S$ values, with values of between 3.6 and 5.6‰ in Units III and VI, and between 6 and 10.2‰ in Units I and II. These values are similar to those recorded in mineralized horizons throughout the Duluth Complex (*e.g.*, Ripley 1981, Ripley & Al-Jassar 1987, Zanko *et al.* 1994). In the Spruce Road area, pyrrhotite and chalcopyrite occur with chlorite in alteration zones (see above) at the contact between the Duluth Complex and the underlying Giants Range Batholith, and are characterized by $\delta^{34}S$

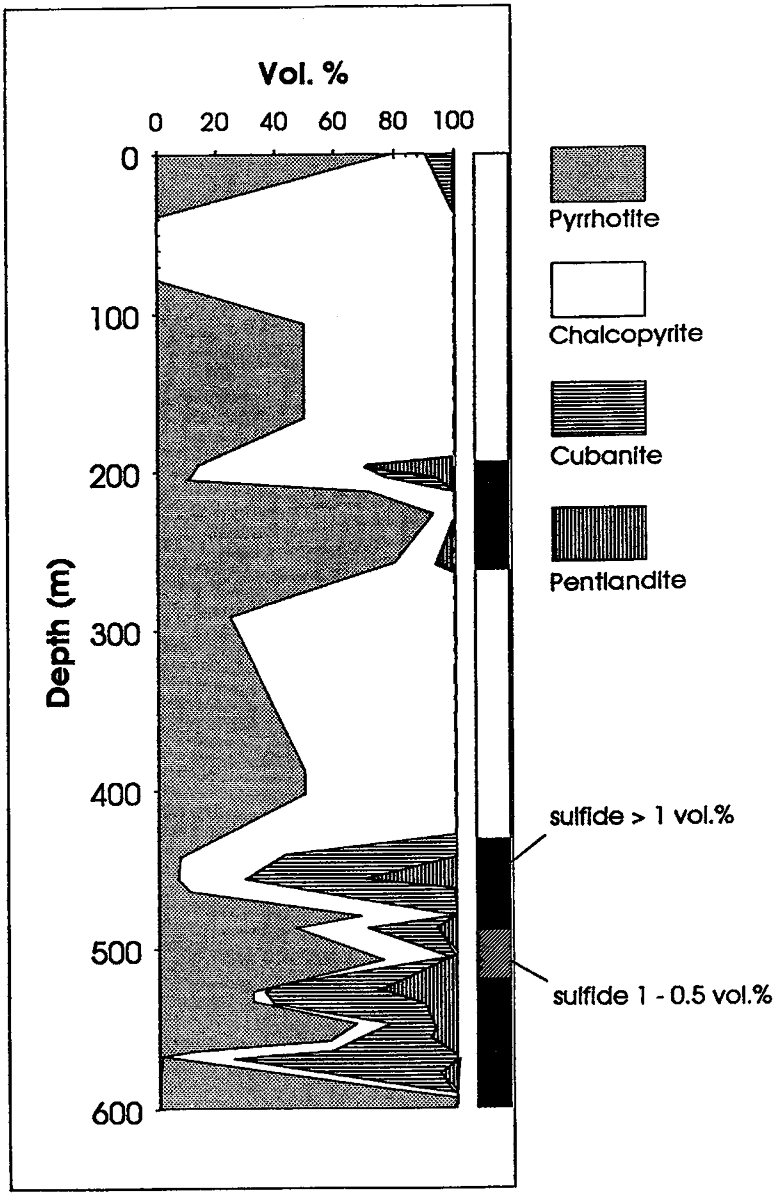

FIG. 5. Modal variations of sulfide minerals in drill core 34870–A.

values of ~9 – 10‰. These sulfides are considered to be derived from those in the Duluth Complex, possibly concentrated by fluid transport along the contact. Similarly, high $\delta^{34}S$ values characterize pyrrhotite-rich veins in other areas of the Giants Range Batholith (Severson 1994). Sulfur concentrations are low in most of the samples obtained from the Giants Range Batholith, and the $\delta^{34}S$ value of the predominant pyrite-rich assemblage is near 0‰.

Sulfur isotope data clearly indicate that mineralized horizons are characterized by ^{34}S enrichment relative to nonmineralized rocks (Fig. 8). Values of $\delta^{34}S$ near 0‰, similar to those from Units IV, V, and VII, are generally taken to be indicative of mantle-derived sulfur. Values of $\delta^{34}S$ in the range of 4 to 10‰ suggest a contribution of ^{34}S-enriched sulfur derived from metasedimentary country-rocks of the Virginia Formation and Biwabik Iron Formation (*cf.* Mainwaring & Naldrett 1977, Ripley 1981, Ripley & Al-Jassar 1987). Although xenoliths of metasedimentary country-rock have been detected in the basal units in the Spruce Road area (Wager *et al.* 1969), the predominance of a granitic footwall suggests that *in situ* derivation of country-rock sulfur is unlikely.

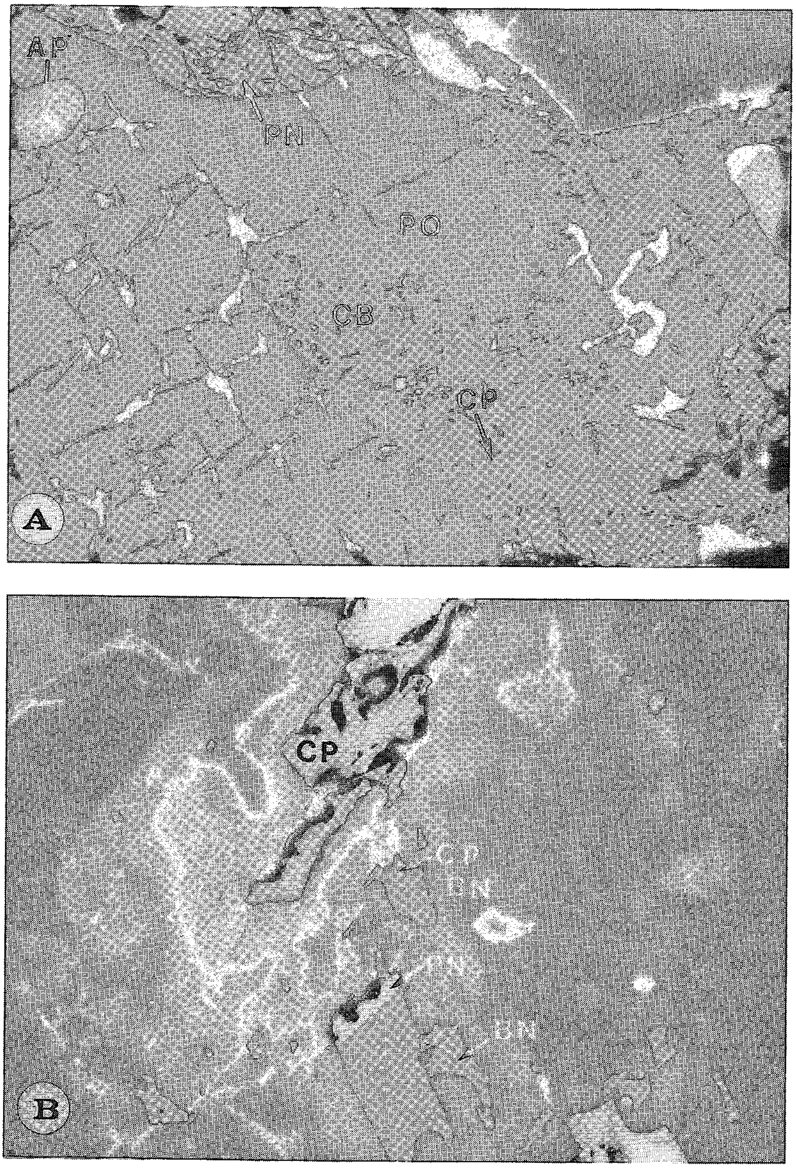

FIG. 6. A. Intergrowth of pyrrhotite (PO), cubanite (CB) with chalcopyrite (CP) lamellae, pentlandite (PN), and apatite (AP). Sample SP3, Unit I, plane light. Field is 1.5 mm wide. B. Disseminated grains of chalcopyrite (CP), bornite (BN) with exsolved chalcopyrite, and pentlandite (PN), associated with biotite. The minerals are located within an interstice between plagioclase grains. Sample SP 306, Unit III, plane light. Field is 0.45 mm wide.

The presence of Virginia Formation and Biwabik Iron Formation xenoliths indicates that these rocks are present at depth, and that magmas must have interacted with them prior to emplacement at their original crustal levels. The difference in isotopic composition between the mineralized units and the overlying sulfide-poor types precludes the possibility that the sulfides accumulated by gravitational settling from overlying magma. Units I–III and VI contain in excess of 0.5 wt.% S, which indicates that their parent melts must have been saturated in sulfide (Haughton *et al.* 1974, Poulson & Ohmoto 1990). Taken together, the data are most consistent with the emplacement of pulses of sulfide-saturated magma that had acquired country-rock sulfur either in a deeper staging chamber, or during ascent.

TABLE 2. SULFUR ISOTOPIC VALUES OF MINERALS AND WHOLE ROCKS FROM DRILL HOLE 34870-A, SOUTH KAWISHIWI INTRUSION, SPRUCE ROAD AREA

Sample Number	Depth (m)	$\delta^{34}S$ (‰ CDT)	Mineral	Comment
SP17	30.5	-0.5	W.R.	
SP36	60.7	1.0	W.R.	
SP54	92.8	-0.4	W.R.	
SP72	118.9	-1.6	W.R.	
SP95	152.4	0.5	W.R.	
SP117	184.1	0.8	W.R.	
SP127	198.3	4.3	Cp+Cb	S.R.
SP133	205.1	3.6	W.R.	S.R.
SP139	213.2	5.5	W.R.	S.R.
SP163	229.1	5.1	W.R.	S.R.
SP185	241.6	5.6	W.R.	S.R.
SP212	259.2	5.3	W.R.	S.R.
SP224	274.5	-0.9	W.R.	
SP234	304.8	2.8	W.R.	
SP242	328.6	-3.4	W.R.	
SP246	340.8	0.2	W.R.	
SP268	397.5	1.2	W.R.	
SP275	413.9	0.3	W.R.	
SP1	443.5	3.9	Po(+Cp)	S.R.
SP292	449.3	3.8	W.R.	S.R.
SP296	457.3	4.1	Cp+Cb	S.R.
SP301	464.0	4.0	W.R.	S.R.
SP306	472.6	5.5	W.R.	S.R.
SP310	480.4	6.9	W.R.	S.R.
SP2	495.9	9.3	Po(+Cp)	S.R.
SP335	526.1	8.0	W.R.	S.R.
SP345	543.5	7.1	W.R.	S.R.
SP347	548.0	10.2	W.R.	S.R.
SP3	559.5	7.7	Cp+Cb	S.R.
SP357	564.5	6.8	Cp+Cb+Po	S.R.
SP6	570.0	6.6	Cp+Cb	S.R.
SP7	578.2	7.6	Cp+Cb+Po	S.R.
SP10	582.5	6.7	Cp+Cb	S.R.
SP371	585.0	7.5	Po(+Cp)	S.R.
SP374	591.9	7.2	W.R.	S.R.
SP394	626.7	9.5	FW Gr	S.R.
SP414	670.3	4.1	FW Gr	
SP425	700.4	0.8	FW Gr	

W.R.: Whole Rock, Cp: Chalcopyrite, Cb: Cubanite, Po: Pyrrhotite, minor amount in parentheses, S.R.: Sulfide > 1 vol%, FW Gr: Footwall granitic rocks

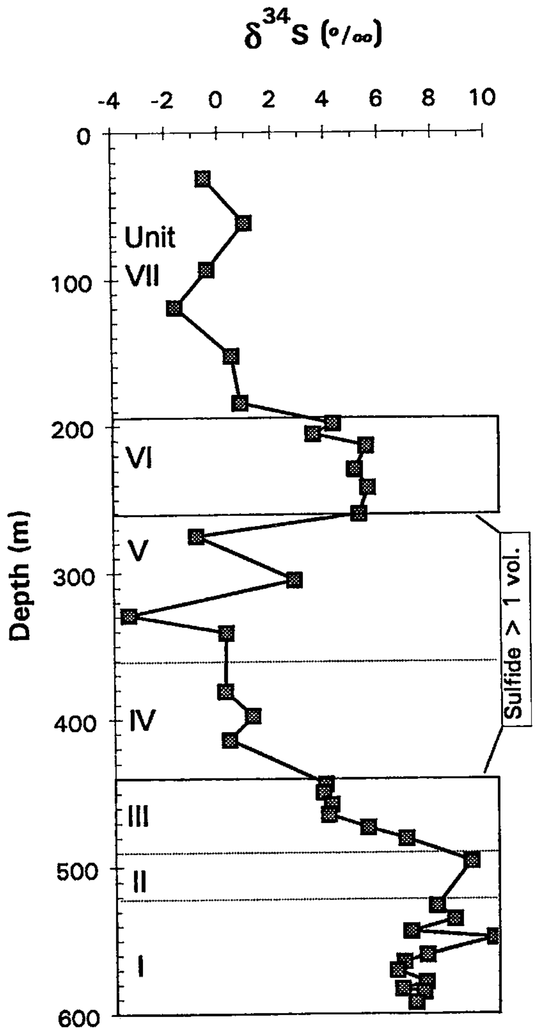

FIG. 7. Sulfur isotopic variation with depth in drill core 34870–A.

In the Babbitt area, within the Partridge River intrusion, Taib & Ripley (1993) have described similar abundances of sulfur isotopes. Sulfide-rich rocks in the Babbitt area are typically relatively evolved, Fe–Ti–P-rich gabbros, and are believed to represent the first melts to be emplaced (Martineau 1989, Severson & Barnes 1991, Chalokwu *et al.* 1993, Taib & Ripley 1993). These melts were contaminated with sulfur in a deeper staging chamber and were sulfide-saturated prior to final intrusion. Troctolitic rock-types that overlie the ferrogabbro in the Babbitt area are characterized by low contents of sulfide and $\delta^{34}S$ values near 0‰. The magmas responsible were more primitive in composition, contained sulfur of magmatic origin, and were emplaced after the more evolved melts (Taib & Ripley 1993). Contamination with sedimentary sulfur did not occur, most likely because country rocks had been desulfurized by previous magmas. A similar interpretation may be applicable to the Spruce Road area sulfides, but the initial pulses of contaminated magma at Spruce Road are not as chemically evolved as the ferrogabbro at Babbitt (Lee & Ripley, in press). However, based on S isotopic data, the melts must have interacted with a similar source of sulfur as did the magmas in the Babbitt area. The most likely mechanisms for sulfur addition are devolatilization of metasedimentary units at depth and localized partial melting. Sulfidic sediments of the Virginia Formation are a likely candidate as a source of sulfur. Numerous pyrrhotite-rich beds in the metamorphosed Virginia Formation are characterized by $\delta^{34}S$ values in the range 0 – 29‰. Sulfides in the Virginia Formation display local increases in $\delta^{34}S$ stratigraphically upward, suggestive of bacterial reduction of sulfate in an envi-

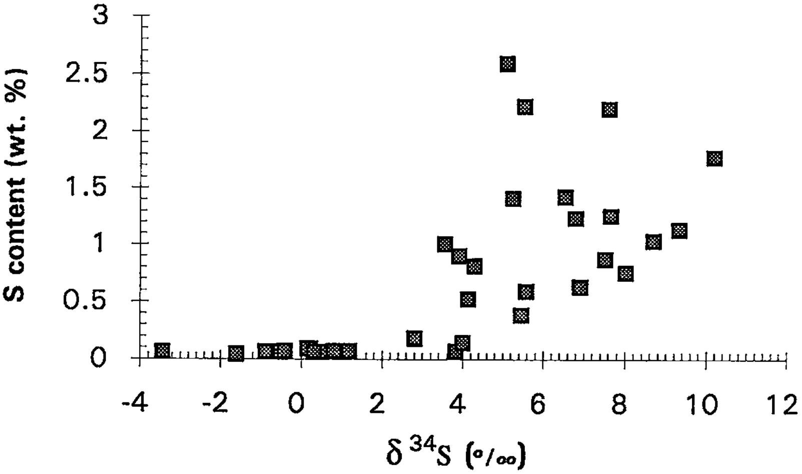

FIG. 8. S content *versus* $\delta^{34}S$ for samples from drill core 34870–A.

ronment where sulfate abundance is limited, probably by basin closure (Zanko *et al.* 1994). For this reason, $\delta^{34}S$ values for pyrite and pyrrhotite in the +6 to +12‰ range are most common in the Virginia Formation, in line with a sulfide origin controlled by bacterial reduction of sulfate following a Rayleigh process.

INTERPRETATION OF CRYSTALLIZATION AND ZONING OF SULFIDE MINERALS

Sulfur contents of Units IV, V, and VII at Spruce Road are generally between 400 and 900 ppm, and are not sufficient to have caused sulfide saturation in the silicate melts at or near liquidus temperatures (Haughton *et al.* 1974, Poulson & Ohmoto 1990). The fine-grained, generally Cu-rich sulfides present in the rocks are associated with interstitial silicates and oxides, a texture consistent with very late-stage saturation in sulfide. Except for local perturbations, Cu abundances display a strong positive correlation with concentrations of lithophile incompatible elements (*e.g.*, Y, P, and Ti; Fig. 9, Table 3). Values of $\delta^{34}S$ (Fig. 7) are typical of mantle-derived sulfides. Other isotopic and chemical indicators (Lee & Ripley, in press) suggest that these rocks formed from magmas that experienced little contamination by crustal rocks. Virtually all textural and geochemical data suggest that the rocks crystallized from pristine, sulfide-undersaturated melts. Emplacement of uncontaminated melts may have occurred during the late stages of plutonism within the mid-continent rift system, at a time when S had been strongly depleted in the metasedimentary successions owing to the earlier intrusion of ferrogabbroic magmas.

In sulfide-bearing Units I, II, III, and VI, distinct compositional variations can be linked to trends in silicate crystallization and differentiation. Lee & Ripley (in press) have proposed that upward increases in concentrations of incompatible elements, along with variations in mineral chemistry, result from a process of boundary-layer crystallization and upward expulsion of residual liquid (*cf.* Langmuir 1989, Nielsen &

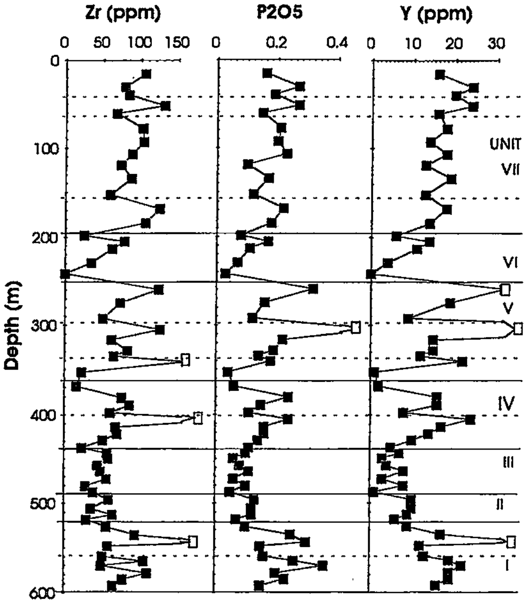

FIG. 9. Variation in the concentration of incompatible elements (Zr, P_2O_5, Y) in drill core 34870–A. Dashed lines separate units into inferred differentiation or mixing cycles as described by Lee & Ripley (in press).

TABLE 3. MINOR AND TRACE ELEMENT CONCENTRATIONS IN SAMPLES FROM DRILL CORE 34870–A

Sample Depth (m)	Rock Type[1]	Cu ppm	Ni ppm	S wt.%	P_2O_5 wt.%	Y ppm	Zr ppm
15.2	T	276	303	–	0.16	16	106
30.5	T	104	172	0.06	0.27	24	79
39.6	T	247	204	–	0.19	20	84
52.1	OPA	164	28	–	0.27	24	132
60.7	T	149	208	0.06	0.15	16	68
77.6	G	145	131	–	0.21	18	103
92.8	T	147	339	0.07	0.20	14	104
106.7	T	186	285	–	0.23	18	89
118.9	T	111	231	0.04	0.10	13	74
134.1	T	165	211	–	0.17	19	88
152.4	T	112	244	0.06	0.12	13	60
168.0	T	208	285	–	0.22	18	126
184.1	T	170	433	0.07	0.18	14	107
198.3	T	4462	1487	0.81	0.08	6	25
205.1	N	9318	1672	1.00	0.17	14	79
213.2	T	2397	449	2.22	0.11	11	63
229.1	T	1721	436	2.59	0.07	4	35
241.6	T	446	143	0.59	0.03	<1	<10
259.2	AN	1991	756	1.41	0.32	32	125
274.5	OG	202	222	0.06	0.16	19	74
292.2	OG	1918	392	0.18	0.12	9	51
304.8	T	122	47	0.06	0.53	84	127
316.4	T	208	200	–	0.22	15	63
328.6	OG	100	116	0.05	0.19	15	84
334.7	OA	181	188	–	0.14	12	66
340.8	OG	251	298	0.09	0.18	22	163
353.0	OA	33	186	–	0.04	1	23
368.5	T	35	174	0.04	0.06	2	16
380.6	T	190	567	0.09	0.24	16	77
389.2	OG	229	500	–	0.15	16	87
397.5	MT	163	586	0.07	0.11	8	61
405.1	AN	189	316	–	0.24	24	221
413.9	OA	72	254	0.06	0.16	17	69
421.8	MT	173	888	0.04	0.16	14	71
429.2	T	88	403	0.05	0.14	10	52
437.3	MT	8297	1747	0.66	0.11	5	24
443.5	T	12497	1248	0.90	0.10	7	58
449.3	T	824	618	0.07	0.06	3	59
457.3	OG	3388	1254	0.52	0.08	4	45
464.0	N	1186	618	0.14	0.11	8	49
472.6	MT	2541	1081	0.38	0.06	3	57
480.4	T	3569	759	0.63	0.10	8	29
487.4	OG	2710	1160	0.41	0.05	1	39
494.9	AN	7611	907	1.13	0.13	10	60
506.1	N	2346	613	0.73	0.12	10	36
512.7	T	3314	659	0.71	0.12	9	65
518.2	N	589	253	0.20	0.07	6	30
526.1	N	5049	1110	0.75	0.10	9	57
535.3	T	3809	1016	1.03	0.25	17	95
543.5	AN	606	281	0.12	0.30	39	205
548.0	OG	6446	1373	1.77	0.15	12	59
559.5	ON	10617	1590	1.25	0.16	13	52
564.5	N	6882	1111	1.23	0.26	19	107
570.0	OG	11911	2375	1.42	0.36	22	50
578.2	N	15481	2481	2.20	0.20	19	112
585.0	N	4089	892	0.87	0.23	19	79
591.9	N	1622	376	0.19	0.15	16	66
606.6	MD	54	22	0.04	0.17	4	43
626.7	MD	17887	1409	–	0.13	5	284
643.1	QM	6	9	0.04	0.02	14	84
670.3	M	461	96	–	0.24	10	151
700.4	MD	80	4	–	0.21	32	453
732.7	GD	30	6	–	0.05	41	119

1. Rock types: MT, mela-troctolite; T, troctolite; OG, olivine gabbro; G, gabbro; N, norite; AN, augite norite; OA, olivine anorthosite; OPA, orthopyroxene anorthosite; MD, monzo-diorite; QM, quartz monzonite; M, monzonite; GD, granodiorite. (–) = not determined.

DeLong 1992). In each mineralized unit, Cu and Ni contents tend to increase upward within a differentiation cycle. A pyrrhotite-rich interval is overlain by a cubanite–chalcopyrite-rich interval in Units I, II, and VI. Both Cu and Ni values are clearly enriched relative to incompatible elements such as Y and Zr (Fig. 9), but

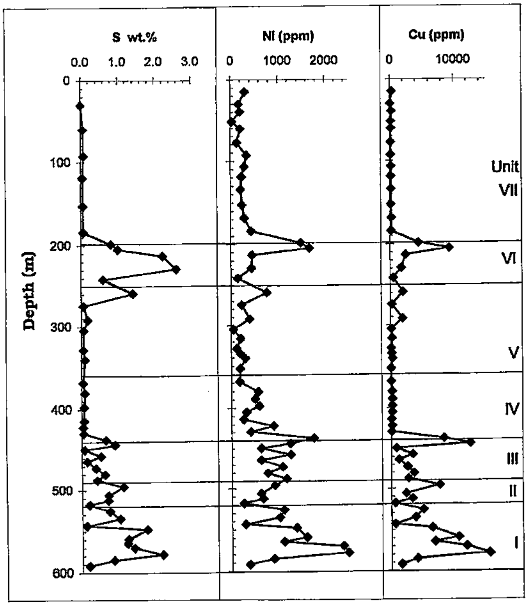

FIG. 10. Variations in whole-rock Cu, Ni, and S contents in drill core 34870–A.

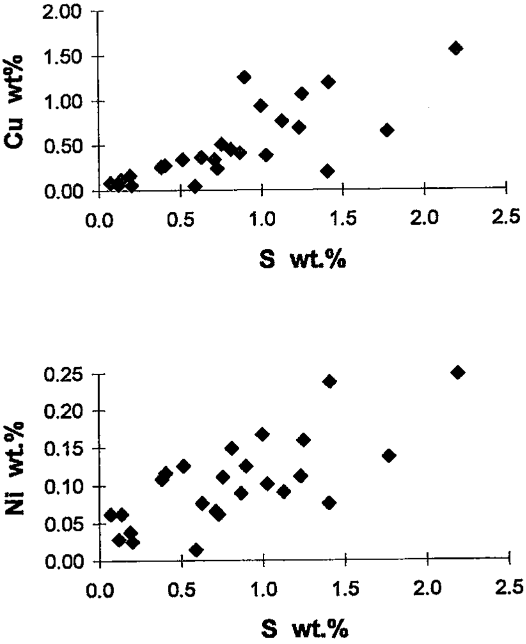

FIG. 11. Crossplots of Cu and Ni contents *versus* sulfur (wt.%) for samples with greater than or equal to 0.12 wt.% S. Samples with high sulfur, but low Cu or Ni content, are pyrrhotite-rich.

they follow the same pattern of upward increase in concentration (Fig. 10). Although Cu and Ni contents increase upward within each cycle, S does not always show a sympathetic relationship (Figs. 10, 11). These compositional trends are explicable in terms of the bulk composition of a sulfide liquid in the initial melts, extent of prior crystallization of pyrrhotite, and a model of boundary-layer fractionation.

Kullerud *et al.* (1969) discussed the crystallization of a sulfide liquid in terms of the ternary systems Cu–Fe–S, Fe–Ni–S, and Cu–Ni–S. According to their experiments, Fe-rich monosufide solid-solution (*mss*) is the first phase to crystallize from a series of compositions similar to those of many mafic-rock-hosted ore deposits. A Cu- and Ni-enriched liquid may coexist with the *mss* at temperatures above ~1000°C. The presence of a Ni-enriched liquid in equilibrium with *mss* has recently been verified by Fleet *et al.* (1993) and Ebel & Naldrett (1994). Crystallization of a sulfide-saturated silicate melt in a boundary layer would produce *mss*, with Cu- and Ni-enrichment in the residual liquid, which may physically separate from the *mss*. In the mineralized units at Spruce Road, the upward increase in Cu and Ni contents, as well as the mineralogical zoning of sulfide assemblages, are consistent with such a process. The differences between sequences marked by upward increases in Cu, Ni, and S (Unit I, Unit II: Fig. 10), and those with increasing Cu and Ni but decreasing S (Unit VI), would therefore appear to reflect bulk compositions of sulfides and amount of early-crystallizing *mss*. Bulk compositions of sulfide assemblages in each unit based on sulfide norm calculations (Hoffman *et al.* 1979) are given in Table 4. Where FeS is a major component of the sulfide liquid and cumulus *mss* is abundant, sulfur content decreases upward. In each case, Cu and Ni increase upward as a result of accumulation of residual silicate and sulfide liquid. The physical process may be driven by filter-pressing, or may possibly result from a decrease in density related to the accumulation of H_2O in the residual liquid. Where Fe–S complexes are depleted in the postulated initial bulk composition (either owing to compositional controls or prior fractionation of *mss*), and only small amounts of cumulus *mss* accumulate, sulfur content increases upward along with Cu and Ni. In both cases, the trends in Ni abundance are controlled primarily by fractionation of the sulfide liquid, and not by olivine abundance.

TABLE 4. BULK COMPOSITION OF SULFIDE ASSEMBLAGES IN UNITS I, II AND VI BASED ON SULFIDE NORM CALCULATION*

	UNIT I LOWER	UNIT I UPPER	UNIT II	UNIT VI
Po	25.9	60.0	35.1	88.3
Cb+Cp	72.4	39.0	62.5	11.3
Pn	1.7	1.0	2.4	0.4

Po: pyrrhotite, Cb + Cp: cubanite + chalcopyrite, Pn: pentlandite. * In wt.%, after Hoffman *et al.* (1979).

Within Unit III, sulfur content is less than 0.4 wt.%, except near the upper boundary with Unit IV, where Cu and, to a lesser extent, Ni and S increase. The massive oxide layer in Unit III is considered to result from a magma-mixing process, and accumulation of Cu-rich sulfides occurs above this layer. We suggest that the magma added to the resident liquid in Unit III was relatively Cu-rich, and that *in situ* crystallization produced a layer of Cu-rich sulfide near the top of the unit.

INTERPRETATION OF Cu-, Ni-, AND ^{34}S-ENRICHMENT

Models of *in situ* crystallization are informative with respect to Cu–Ni distribution and mineralogical zoning within intrusive units. However, the thickness of each mineralized unit (<80 m), together with the clear distinction in $\delta^{34}S$ values between mineralized and unmineralized units, strongly suggest that *in situ* processes of fractionation cannot explain the Cu–Ni enrichment. Models to explain the Cu–Ni mineralization at Spruce Road, as well as the majority of sulfide mineralization in the Duluth Complex, must focus on processes of Cu–Ni enrichment that occur in staging chambers, and must explain elevated $\delta^{34}S$ values in the range of +4 to +10‰.

Rao & Ripley (1983) and Ripley (1993) have presented models of Cu-enrichment in mantle-derived melts caused by fractional crystallization in staging chambers augmented by magma recharge and blending. O'Hara & Matthews (1981) presented models of enrichment in incompatible elements in magma chambers caused by periodic recharge. Where coupled with convective fractionation of incompatible-element-rich residual liquids, an effective means of magma enrichment results. If Cu is treated as a perfectly incompatible element, the enrichment during fractional crystallization of a parental magma can be computed by:

$$C = \frac{C_0}{1 - F}$$

where C is the concentration of Cu, C_0 is the initial Cu content (taken as 200 ppm), and F is the fraction crystallized. Assuming 80% fractional crystallization of olivine, plagioclase, and minor spinel, a sulfide-saturated magma with ~1000 ppm Cu may be produced. Periodic addition of magma that is similar in composition to the unfractionated parent (200 ppm Cu) would lead to further Cu-enrichment (Rao & Ripley 1983, Ripley 1993), and emplacement of such a Cu-enriched magma may explain horizons of low-grade mineralization. However, it is difficult to model mineralized zones of 0.5 to 1.0 wt.% Cu, similar to those that occur throughout the Duluth Complex, by such a process.

Magmatic concentration of Cu+Ni via settling of immiscible sulfide liquids

A more likely alternative to *in situ* concentration processes involves sulfide immiscibility and gravitational collection of sulfide at depth within a staging chamber, followed by emplacement of sulfide-saturated, Cu–Ni-enriched magma. A similar model has been proposed by Naldrett (1992), Naldrett *et al.* (1992), and Brügmann *et al.* (1993) for the Noril'sk deposits in the Siberian flood basalt province. Their model calls upon sulfide saturation in the upper portions of a fault-controlled magma system at depth caused by introduction of ^{34}S-enriched country-rock sulfur. A zone-refining model is envisioned where the descending sulfide scavenges additional metal from sulfide-undersaturated melt below. Ore-bearing intrusive bodies result from the emplacement of magma at the base of the chamber that had been enriched by the accumulated sulfide. Ore-barren, sulfide-poor intrusions are considered to be derived from overlying liquid in the chamber that had been depleted of its metal content, and periodically mixed with new, uncontaminated magma that intruded the chamber. We propose a model that differs from that of Naldrett (1992) principally in the smaller size of the staging chamber, and in a more uniform attainment of sulfide saturation in the chamber. In such a model, sulfide-depleted, contaminated magma in the chamber also would be characterized by elevated δ^{34}S values derived from ^{34}S-enriched metasedimentary country-rocks.

As a numerical example, a spinel lherzolite mantle source with ~20 ppm Cu, 2000 ppm Ni, and 200 ppm S (Morgan *et al.* 1981, Sun 1982) is utilized. At the mantle source, a minimum of 80% of the copper is assumed to be sulfur-bonded, whereas 20% is held in silicates such as clinopyroxene. Approximately 1.9% of the nickel in the mantle source is held as sulfide, based on average concentrations of pentlandite and pyrrhotite and a chalcopyrite/pentlandite ratio of ~1:3 in mantle xenoliths (*e.g.*, Lorand 1989, Anderson *et al.* 1987). Additional parameters used for the calculation are given in Table 5. Batch partial melting of 20% of the mantle source with complete melting of sulfide minerals yields a derivative melt with ~76 ppm Cu (65 ppm from sulfide, 11 ppm from silicate), 687 ppm Ni (235 ppm from sulfide, 452 ppm from silicate), and a total S content of ~1000 ppm. In order to produce the high-Al olivine tholeiitic melts that seem to be parental to much of the Duluth Complex, extensive fractional crystallization of a primary melt is required (*e.g.*, Klewin 1989). During this process, the concentrations of chalcophile metals and sulfur increase, and sulfur concentration may exceed the saturation limit. Data from Wendlandt (1982) indicate that in deep chambers, sulfur solubility in mafic magmas is ~1500 ppm. Metal and sulfur depletion of the derivative magma in deep staging chambers is therefore expected.

A depletion of chalcophile elements within some magmas emplaced into the rift system is strongly suggested by a review of the compositions of lavas of the North Shore Volcanic Group. In particular, highly evolved Fe–Ti–P-rich basalts that characterize the early stages of volcanism in the rift (*e.g.*, Green *et al.* 1987, Brannon 1984) may be produced by 75 to 85% fractionation of high-Al olivine tholeiite compositions, as reviewed by Miller & Weiblen (1990). Although lithophile elements such as Zr and Y, as well as P and Ti, are predictably high in the lavas, abundances of

TABLE 5. RESULTS AND SUMMARY OF PARAMETERS USED TO CALCULATE THE Cu AND Ni CONTENT OF A MELT PRODUCED BY 20% BATCH PARTIAL MELTING OF A SPINEL LHERZOLITE, WITH COMPLETE DISSOLUTION OF SULFIDE

Mineralogy[1]	wt.%	$D^{Cu}_{min/melt}$[2]	$D^{Ni}_{min/melt}$[3]	Cu(ppm from silicate)	Cu(ppm from sulfide)	ΣCu_{melt}	Ni(ppm from sulfide)	Ni(ppm from silicate)	ΣNi_{melt}
ol	50					76		452	687
opx	21								
cpx	23	2	2	11					
sp	5	12							
sulfide	.055				65		235		

Contents of Ni, Cu, and S in the mantle source are 2000 ppm, 20 ppm, and 200 ppm, respectively.

[1] Silicates and spinel from Miller (1986)

[2] $D^{Ni}_{min/melt}$ for ol, opx, and cpx from Duke and Naldrett (1978); for sp from Seward (1971).

[3] $D^{Cu}_{min/melt}$ for cpx from Seward (1971)

chalcophile elements are low (Cu contents ~200 ppm rather than 800 – 1300 ppm). This evidence suggests that sulfide segregation may have occurred within deep staging chambers. Magma recharge and blending that accompanied fractional crystallization in the chambers would serve to elevate abundances of the chalcophile elements, and, together with sulfide accumulation, provide an efficient mechanism for the production of chalcophile-element-enriched magmas. Sulfide depletion in deep magma chambers also has been postulated by Saini-Eidukat (1991) on the basis of abundances of the PGE and base metals in rocks of both the troctolitic and anorthositic series.

Sulfide depletion of fractionating melts is a very important concept in understanding the production of high-^{34}S mineralization in the Duluth Complex. Simple mass-balance calculations assuming a magma density in the range of 2.7 to 2.8 g/cm^3 indicate that to account for a 50-m-thick mineralized unit such as Unit I, a magma chamber with a minimum vertical extent of ~1500 m is required (this assumes nearly complete extraction and accumulation of Cu). A mass ratio of silicate magma to sulfide magma (R value of Campbell & Naldrett 1979) of ~700 is computed, and is consistent with the overall composition of sulfide assemblages at Spruce Road, which average 10 to 14% Cu and 1 to 3% Ni. It is therefore possible to simulate the formation of sulfide minerals at Spruce Road with mathematical models that describe gravitational settling of magmatic sulfides in a deep staging chamber, followed by emplacement of the sulfide-enriched melt. However, this approach cannot explain the elevated δ^{34}S values, nor the depletion in PGE discussed by Saini-Eidukat (1991). A more likely model involves the addition of externally derived sulfur to a shallower chamber that contains chalcophile-metal-depleted melt. Sulfide-poor rocks in the Spruce Road area and throughout the Duluth Complex are characterized by δ^{34}S values near 0‰. These rocks show little or no evidence of crustal contamination, and their sulfide δ^{34}S values are considered to be near the values of the primitive mantle. The contaminant sulfur likely derived from metasedimentary country-rocks is taken to have an average δ^{34}S value of ~10‰ (*e.g.*, Ripley & Al-Jassar 1987, Zanko *et al.* 1994). Mass-balance computations suggest the involvement of 30 to 70% externally derived sulfur in the mineralization at Spruce Road.

Externally derived sulfur must bond with metals initially present in metal-depleted melt derived from the deeper chamber as silicate or oxide complexes, or as neutral species, to account for the Cu–Ni enrichment. In the spinel lherzolite model system, 20% of the initial copper is present in a silicate form, primarily clinopyroxene. Reaction between Cu_2O (or similar complexes) produced during partial melting, NiO, and

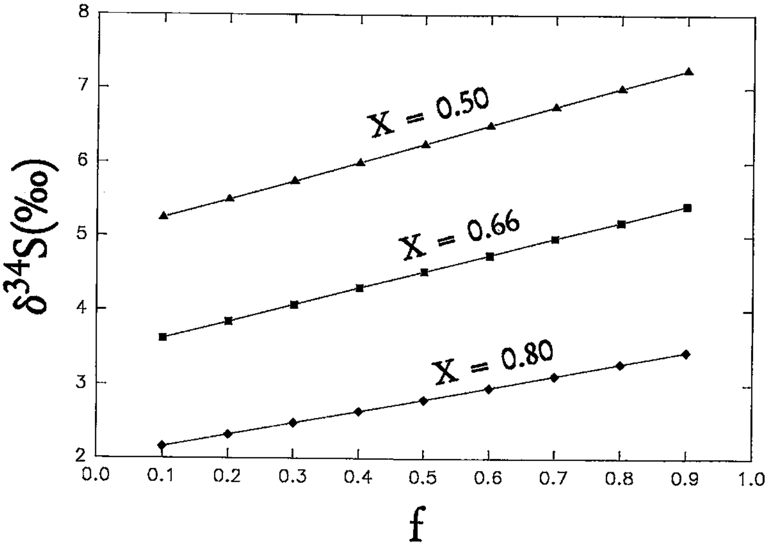

FIG. 12. Plot of δ^{34}S values of a magma *versus* fraction of Cu that is bonded to mantle sulfur that crystallizes at depth in a staging chamber (f). The reference volume is 1500 m × 50 m × 50 m, and the parent magma contains 200 ppm Cu. Values of X refer to the proportion of Cu that is bonded to mantle sulfur in the unfractionated parent melt. See text for further details.

external sulfur in a shallower crustal staging chamber produces a second population of sulfides with elevated $\delta^{34}S$ values. A mixture composed of up to 70% mantle-derived sulfur and 30% external sulfur can satisfy the $\delta^{34}S$ mass-balance requirements for assemblages with values of 4–5‰.

Many variations of this type of model are possible. Metals not bonded to sulfur, such as copper, must be available to react with externally derived sulfur if Cu-rich and isotopically anomalous assemblages are expected to be produced. In addition, the sulfur isotopic composition of both the mantle source and the contaminant may be variable. For example, the sulfur isotopic composition of probable contaminant sulfide derived from the Virginia Formation ranges between 0 and 29‰ (Ripley & Al-Jassar 1987, Zanko *et al.* 1994). The vertical extent of the magma chamber necessary to produce the observed concentration of sulfide at Spruce Road may vary from a minimum of ~1500 m, to ~5000 m depending upon the initial Cu content of the parent magma and the extent of depletion of metals bonded with sulfur of mantle origin. If metals bonded with mantle sulfur are strongly depleted during fractional crystallization at depth, a greater mass of magma containing Cu_2O (or similar) complexes is required to react with externally derived sulfur and produce the high-$\delta^{34}S$ mineralization. If metals bonded with mantle sulfur are not strongly fractionated, then less oxide or silicate copper is processed, and $\delta^{34}S$ values are lower. Figure 12 illustrates the variations in $\delta^{34}S$ values of magma in a reference volume *versus* the fraction of Cu bonded to sulfur that crystallizes at depth. The reference volume is 1500 m × 50 m × 50 m, and the magma contains 200 ppm Cu. If concentrated, this amount of Cu is sufficient to produce a 50 m × 50 m × 50 m volume that grades 0.6 wt.% Cu, similar to mineralized units in the South Kawishiwi intrusion. A specified fraction of Cu that is bonded to magmatic sulfur is allowed to crystallize, and a mass of unfractionated magma that contains an equivalent amount of Cu is added. The Cu in the added increment is distributed between sulfide and non-sulfide sites in the same proportions as in the original magma. The governing equations are:

$$Cu^M = Cu^{\circ}_{mag}\,(1 - f + xf)$$
$$Cu^S = Cu^{\circ}_{sil} + Cu^{\circ}_{mag}\,(y)(f)$$

where Cu^M represents the concentration of Cu in the silicate melt that is bonded with magmatic S, Cu^S is the concentration of Cu in the silicate melt that is not bonded with sulfur, Cu°_{mag} is the initial concentration of Cu in the silicate melt that is bonded with mantle S, Cu°_{sil} is the initial concentration of Cu in the silicate melt that is not bonded with S, f represents the fraction of Cu bonded with mantle S that crystallizes at depth, x is the fraction of Cu in the unfractionated magma that is bonded to mantle S, and y is the fraction of non-S bonded Cu in the unfractionated magma. Values of 0‰ and 10‰ are assumed for mantle and external sulfur, respectively, and the bulk composition of the sulfide-saturated liquid that could be emplaced at shallow depths is estimated by:

$$\delta^{34}S_{bulk}(‰) = \frac{Cu^M}{Cu^S + Cu^M} \times 10$$

We believe that only limited fractionation of sulfide occurred in the more primitive melts that produced Units III and VI, and for this reason their $\delta^{34}S$ values are lower than in Units I and II.

Concentration of Cu + Ni by hydrothermal fluid

A second method to explain the origin of the sulfide mineralization at Spruce Road is *via* hydrous fluids that have concentrated metals leached from large volumes of rock. Although only Unit VI shows signs of extensive hydrothermal alteration, sulfide minerals in this unit are not intergrown with secondary minerals. It is unclear as to why Unit VI appears to have been permeable to late-stage fluids, but sulfides are only rarely recognized as being related to the alteration. Extensive alteration is not observed in Units I, II, or III, and it is suggested that low-temperature secondary mineralization did not develop in these units.

Boudreau & McCallum (1992) have modeled the processes of hydrothermal enrichment in magmas that may lead to formation of PGE-rich reefs such as those in the Stillwater and Bushveld complexes. Metal enrichment is achieved by upward movement of Cl-rich fluids derived from intercumulus melt. Metals and sulfur are leached by the fluids and may redissolve in overlying, hotter, fluid-undersaturated melt. A dynamic system is envisioned as the now metal-enriched melt becomes fluid-saturated after extensive crystallization, and exsolves fluid that continues upward to extract additional metal and sulfur. Deposition may occur when a stratigraphic discontinuity is encountered, resulting in a laterally continuous stratiform ore-zone. It is clear from the presence of sulfide-enriched basal units at Spruce Road that such a process cannot explain the mineralization in its present form. However, the Boudreau & McCallum (1992) model bears similarities to models of upward enrichment in chalcophile elements caused by fractional crystallization and magma blending (Ripley 1993), but adds to it the potential for more efficient extraction of metal and sulfur by leaching of previously crystallized sulfide. If the magma in a staging chamber is differentiating *via* boundary-layer fractionation, as described by Nielsen & DeLong (1992), extraction of overlying melt after the metal-sulfide-rich fluid derived from underlying cumulates had dissolved, could lead to metal-enriched units such as those at Spruce Road. The process accomplishes the same end as downward accumulation of immiscible sulfide liquid, and also would be limited by the $\delta^{34}S$ requirement that 30–70% of the initial sulfide be of external origin. A process of this type does not remove the requirement that an early stage of sulfide segregation must have occurred in deep chambers.

External addition of sulfur and metals

A third method for producing metal enrichment and elevated $\delta^{34}S$ values involves external addition of both metals and sulfur. Some metal-rich black shales are known to be enriched in Cu, Ni, and PGE (*e.g.*, Ripley *et al.* 1990, Coveney *et al.* 1991, Hulbert *et al.* 1992). Our previous studies (Ripley 1986) suggested little or no depletion in chalcophile elements within metamorphosed Virginia Formation, but these studies were restricted to pelitic rocks near the basal contact with mineralized troctolitic rocks. It is possible that in deeper settings, dehydration as well as partial melting of the sedimentary country-rock could lead to extraction of metal as well as sulfur from the sediments. Such a model was proposed by Tyson & Chang (1984), and may warrant further investigation.

CONCLUSIONS

Results of mineralogical and geochemical studies of sulfide mineralization in the South Kawishiwi intrusion in the Spruce Road area can be summarized as follows:
1) Sulfide mineralization, consisting of 1 to 5 volume % of disseminated pyrrhotite, cubanite, chalcopyrite, and pentlandite, occurs in Units I, II, III, and VI. Within Units I, II, and VI, layers rich in pyrrhotite are overlain by layers rich in cubanite + chalcopyrite.
2) Values of $\delta^{34}S$ in mineralized rock-types range from 3.8 to 10.2‰, and are distinctly different from those of non-mineralized rocks, which range from –3.4 to +2.8‰. Both the sulfide mineralogy and $\delta^{34}S$ systematics are similar to those of mineralized units in the Partridge River intrusion, and suggest that metasedimentary country-rocks are present at depth, and that sulfur addition and sulfide liquid immiscibility occurred in shallow crustal staging chambers, rather than *in situ*.
3) The observed upward enrichment of Cu and Ni concentrations and sulfide mineralogical zoning within Units I–II and VI can be modeled mathematically by *in situ* crystallization and upward expulsion of residual liquid. However, the observed overall enrichment of Cu and Ni cannot be easily explained by *in situ* processes. The emplacement of metal-enriched magmas that were derived from deeper staging chambers is indicated. Addition of at least 30% crustal sulfur is required to explain the $\delta^{34}S$ values of the mineralized units. Sulfide mineralization in Units I, II, III, and VI is believed to have resulted from the emplacement of multiple batches of sulfide-saturated basaltic magmas that had experienced varying degrees of silicate and sulfide fractionation.

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