

COMPOSITIONAL VARIATIONS IN Cu–Ni–PGE SULFIDES OF THE DUNKA ROAD DEPOSIT, DULUTH COMPLEX, MINNESOTA: THE IMPORTANCE OF COMBINED ASSIMILATION AND MAGMATIC PROCESSES

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ABSTRACT

The Dunka Road deposit is one of ten occurrences of Cu–Ni sulfides bearing platinum-group elements (PGE) on the northwestern margin of the Duluth Complex, in Minnesota. Mineralization has been linked to contamination of the host troctolitic magma through assimilation of argillaceous rocks from the Virginia Formation. On the basis of texture and composition, the sulfide mineralization is divided into five types: 1) norite-hosted disseminated sulfides, 2) troctolite-hosted disseminated sulfides, 3) PGE-rich disseminated sulfide horizons, 4) pyrrhotite-rich massive sulfides, and 5) chalcopyrite-rich disseminated sulfides. The norite-hosted sulfides exhibit features suggestive of the magma's substantial contamination, such as high proportions of pyrrhotite and arsenide minerals, and high mean values of S/Se (9,700) and $\delta^{34}\text{S}$ (11.2‰). They are also generally metal-poor, implying that the sulfides interacted with a relatively low volume of silicate melt (*i.e.*, low *R* factor). The troctolite-hosted sulfides formed at moderate degrees of contamination, as indicated by their intermediate mean values of S/Se (4,600) and $\delta^{34}\text{S}$ (7.8‰). The PGE-rich sulfide horizons show little sign of contamination, and have mantle-like mean values of S/Se (2,600) and $\delta^{34}\text{S}$ (2.1‰). Their very high PGE contents suggest that they formed at elevated *R* factors. The pyrrhotite-rich massive sulfides and associated chalcopyrite-rich disseminated sulfides have relatively high mean values of S/Se (8,000) and $\delta^{34}\text{S}$ (10.2‰), indicative of significant contamination. The former are interpreted to represent a cumulate of monosulfide solid-solution (*mss*), whereas the chalcopyrite-rich sulfides represent the fractionated sulfide liquid. A general increase in the degree of contamination is observed toward the base of the intrusion, associated with a decrease in *R* factor and metal concentration of the sulfides. This likely results from the introduction of partial melt from the metasedimentary country-rocks, which was cooler than the mafic magma and led to the early crystallization of the sulfide liquid.

Keywords: sulfide deposits, assimilation, sulfur isotopes, S/Se ratios, *R* factor, *mss* fractionation, troctolite, platinum-group elements, nickel, copper, arsenides, Dunka Road deposit, Duluth Complex, Minnesota.

SOMMAIRE

Le gisement de Dunka Road fait partie d'un groupe de dix gisements de sulfures de Cu–Ni enrichis en éléments du groupe du platine (EGP) regroupés le long de la bordure nord-ouest du complexe de Duluth, au Minnesota. La minéralisation serait liée à une contamination du magma-hôte troctolitique due à une assimilation de roches argileuses de la formation de Virginia. D'après leur texture et leur composition, les sulfures sont divisés en cinq types: 1) sulfures disséminés dans la norite comme hôte, 2) sulfures disséminés dans la troctolite comme hôte, 3) horizons de sulfures disséminés enrichis en EGP, 4) sulfures massifs enrichis en pyrrhotite, et 5) sulfures disséminés enrichis en chalcopyrite. Les caractéristiques des sulfures dans la norite, par exemple les proportions élevées de pyrrhotite et de minéraux arsénifères, et des valeurs moyennes élevées de S/Se (9 700) et $\delta^{34}\text{S}$ (11.2‰), font penser que le magma a subi une importante contamination. De plus, ces sulfures sont généralement appauvris en métaux, ce qui implique qu'ils ont réagi avec un faible volume de magma silicaté (*i.e.*, faible facteur *R*). Les sulfures dans la troctolite se sont formés à des niveaux moyens de contamination, tel qu'indiqué par leurs valeurs moyennes intermédiaires de S/Se (4 600) et $\delta^{34}\text{S}$ (7.8‰). Les horizons de sulfures enrichis en EGP montrent très peu de signes de contamination, et ont des valeurs moyennes de S/Se (2 600) et $\delta^{34}\text{S}$ (2.1‰) qui rappellent celles du manteau. Leur très forte teneur en EGP témoigne de facteurs *R* élevés. Les sulfures massifs enrichis en pyrrhotite, et les sulfures disséminés enrichis en chalcopyrite avec lesquels ils sont associés, ont des valeurs moyennes relativement élevées de S/Se (8 000) et $\delta^{34}\text{S}$ (10.2‰), indications d'une importante contamination. Les sulfures massifs résulteraient d'une accumulation d'une solution solide de monosulfure (*mss*), alors que les sulfures enrichis en chalcopyrite représentent un liquide sulfuré fractionné. Une augmentation générale du degré de contamination est observée vers la base de l'intrusion, associée à une diminution du facteur *R* et de la concentration en métaux des sulfures. Ceci résulte possiblement de l'introduction d'un produit de fusion partielle dérivé des roches métasédimentaires encaissantes, moins chaud que le magma mafique, qui aurait ainsi mené à la cristallisation hâtive du liquide sulfuré.

Mots-clés: gisement de sulfures, assimilation, isotopes de soufre, rapports S/Se, facteur *R*, fractionnement de *mss*, troctolite, complexe de Duluth, éléments du groupe du platine, nickel, cuivre, arsénifères, gisement de Dunka Road, complexe de Duluth, Minnesota.

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INTRODUCTION

Most studies of the Duluth Complex have focussed on the Cu–Ni–PGE sulfide deposits that occur along the base of troctolitic intrusions (Thériault *et al.* 1997, and references therein). Country-rock assimilation is widely recognized as having played a significant role in the genesis of the mineralization. Evidence of assimilation is based on stable isotopes (Mainwaring & Naldrett 1977, Ripley 1981, 1986, Rao & Ripley 1983, Ripley & Al-Jassar 1987, Ripley *et al.* 1993, Lee & Ripley 1995), Se/S ratios (Ripley 1990a, Thériault *et al.* 1997), major- and trace-element geochemistry (Tyson & Chang 1984, Ripley & Alawi 1988, Severson & Hauck 1990) and silicate mineralogy (Foose & Weiblen 1986, Geerts 1991).

Although the categories of sulfide occurrences in the Duluth Complex have previously been defined (*e.g.*, Foose & Weiblen 1986, Martineau 1989), no systematic description and classification of the different types of mineralization forming a deposit have ever been attempted. This situation may explain the general lack of agreement concerning the mechanisms of concentration involved in ore formation. In particular, models involving both magmatic and hydrothermal processes have been proposed to explain the localization of platinum-group elements (PGE) in the Duluth Complex.

In this paper, we describe the mode of occurrence of five types of sulfide mineralization observed near the base of the Duluth Complex in the Dunka Road area. We show that compositional variation among the types of mineralization results from the sequential action of three processes, namely country-rock assimilation, interaction between the sulfide liquid and the silicate melt (*R* factor), and fractional crystallization of the sulfide liquid.

GEOLOGICAL SETTING

The Duluth Complex consists of an arcuate mass of mafic intrusions of Middle Proterozoic age (1100 Ma) associated with the Keweenaw flood basalt province of the Midcontinent Rift of North America (Van Schmus & Hinze 1985). The complex extends for more than 225 km along the northwestern margin of Lake Superior, from Duluth, Minnesota, to the Canadian border (Fig. 1). It was emplaced as a succession of distinct mafic intrusions along an unconformity between volcanic rocks of the North Shore Volcanic Group and older Proterozoic (1800–2300 Ma: Hemming *et al.* 1995) basement rocks of the Animikie Group. In general, rocks forming the Duluth Complex consist of an upper anorthositic series underlain by a more mafic troctolitic series (Taylor 1964, Weiblen & Morey 1980). Recent U–Pb ages (1098.6 ± 0.5 to 1099.3 ± 0.3 Ma) obtained by Paces & Miller (1993) suggest that both intrusive series are essentially coeval.

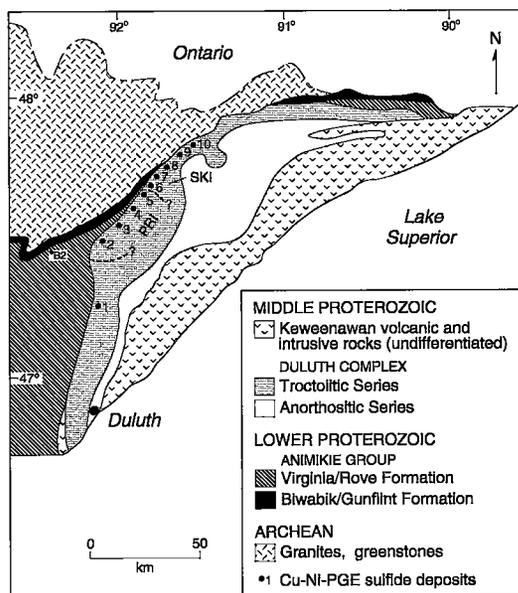


FIG. 1. Geological map showing the emplacement of the Duluth Complex and associated sulfide mineralization within the Keweenaw flood basalt province of central North America (modified after Naldrett 1989). PRI: Partridge River intrusion, SKI: South Kawishiwi intrusion. Black circles represent Cu–Ni–PGE sulfide deposits (1: Water Hen; 2: Wyman Creek; 3: Wetlegs; 4: Dunka Road; 5: Babbitt; 6: Serpentine; 7: Dunka Pit; 8: Birch Lake; 9: Maturi; 10: Spruce Road); B2: drill hole from the Mesabi deep-drilling project.

Significant Cu–Ni–PGE sulfide mineralization has been observed in the basal portions of two of the troctolitic intrusions, namely the Partridge River and South Kawishiwi intrusions (Severson & Hauck 1990, Severson 1994). These are the host to more than 6 billion tonnes of mineralization grading 0.66% Cu and 0.2% Ni (Listerud & Meineke 1977, Ripley 1990b). The sulfide-bearing troctolitic intrusions occur along the northwestern margin of the complex, where they intrude Proterozoic metasedimentary rocks of the Virginia and Biwabik formations (Fig. 1). The latter is a cherty and slaty banded iron-formation (Morey 1992), whereas the overlying Virginia Formation consists mainly of argillite, siltstone, and greywacke. The argillaceous horizons commonly contain finely disseminated pyrite, especially in proximity to the Biwabik Formation (Lucente & Morey 1983).

ANALYTICAL METHODS

Rock samples for this work were taken from drill core provided by the Minnesota Department of Natural

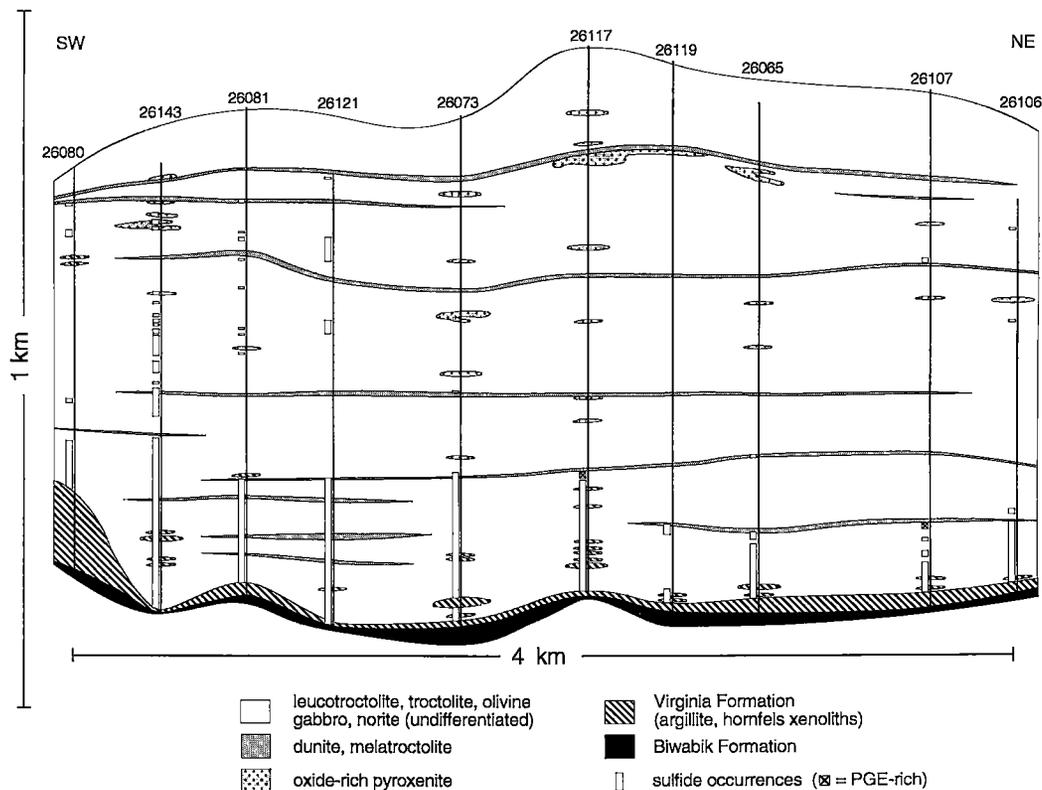


FIG. 2. Longitudinal cross-section of the Dunka Road Cu-Ni-PGE deposit, based on drill-hole interpretation (modified after Severson & Hauck 1990).

Resources, Hibbing, Minnesota. Mineralized samples of the Dunka Road deposit were collected from drill holes #26107, 26117 and 26143 (Fig. 2, Table 1), whereas argillite samples of the Virginia Formation were taken from hole #B2 (Fig. 1, Table 1), which is located approximately 40 km to the southwest of the Dunka Road deposit and well beyond the metamorphic aureole of the complex.

A total of 28 whole-rock samples were analyzed for S, Ni and Cu by X-ray fluorescence spectrometry at Analabs - Caleb Brett in England. Concentrations of the trace elements Co, As, Sb, Se and Au were determined by instrumental neutron-activation analysis (INAA) at the Université du Québec à Chicoutimi using the method of Bédard & Barnes (1990). Samples with a low level of Se were further analyzed for this element by atomic absorption at Chemex Laboratories in Vancouver. Concentrations of the PGE and Re were determined by INAA in Chicoutimi, after precon-

centrating the metals into a Ni-sulfide bead following the method of Robert *et al.* (1971).

The ratio of sulfur isotopes was determined on 24 whole-rock samples by mass spectrometry at the Ottawa-Carleton Geoscience Centre in Ottawa. An additional four measurements were obtained from mineral separates at Indiana University.

GEOLOGY OF THE DUNKA ROAD DEPOSIT

The Dunka Road Cu-Ni-PGE deposit occurs within the basal part of the Partridge River intrusion, where the host mafic rocks are in contact with sulfide-bearing argillites of the underlying Virginia Formation (Fig. 1). As shown from a drill-hole-interpreted cross-section (Fig. 2), the igneous stratigraphy has been subdivided into correlatable cyclic units (Severson & Hauck 1990, Thériault *et al.* 1997). Each cyclic unit consists of a thin ultramafic layer of melatroctolite to dunite overlain

TABLE 1. WHOLE-ROCK METAL CONCENTRATIONS AND SULFUR ISOTOPE VALUES OF THE FIVE TYPES OF SULFIDE MINERALIZATION, THE BEDDED PYRRHOTITE UNIT AND UNMETAMORPHOSED ARGILLITE OF THE VIRGINIA FORMATION

Sample number	Rock type	Drill hole number	Depth (m)	S (%)	Os (ppb)	Ir (ppb)	Ru (ppb)	Rh (ppb)	Pt (ppb)	Pd (ppb)	Au (ppb)	Re (ppb)	Ni (ppm)	Cu (ppm)	Co (ppm)	As (ppm)	Sb (ppm)	Se (ppm)	$\delta^{34}\text{S}$ (‰)	S/Se
DC-27	NOR	26117	708.3	0.77	<6	0.28	<5.0	0.74	13	23	11	0.86	348	1300	114	12.9	0.89	0.6	14.5	13000
DC-49	NOR	26117	727.5	0.20	<5	0.10	<5.0	<21	2.5	5.4	<3.2	0.22	151	373	52	1.96	1.59	<0.2	8.2	>10000
DC-52	NOR	outcrop	—	0.66	<9	0.25	<5.0	0.53	3.7	11	<3.2	0.93	186	293	40	6.28	1.35	0.6	13.7	11000
DC-54	NOR	outcrop	—	0.31	<8	0.22	<5.0	0.46	6.9	8.1	2.3	1.24	265	622	62	2.77	0.80	0.6	12.5	5200
DC-60	NOR	26117	683.4	1.57	<1.3	1.20	<5.0	3.96	50	100	19	2.70	1140	3000	127	3.42	0.57	1.0	10.4	16000
DC-63	NOR	26143	252.3	2.45	<1.2	0.92	<5.0	2.65	16	63	18	4.92	824	2210	180	6.76	0.57	2.2	7.1	11000
DC-66	NOR	26107	721.7	4.32	2.2	4.28	20	18.8	35	460	45	26.8	2280	6400	310	15.5	0.71	5.9	9.8	7300
DC-72	NOR	26117	703.5	4.65	1.3	1.46	<5.0	4.72	5.4	120	45	2.82	1140	3700	290	37.6	0.58	9.6	13.6	4800
DC-53	TROC	26117	741.2	0.15	<8	0.57	<5.0	1.24	12	39	<2.1	0.46	230	514	55	2.23	1.03	0.2	6.7	7500
DC-55	TROC	26117	753.9	1.11	<9	1.01	6.9	4.17	42	170	32	3.57	1070	3650	89	1.58	1.51	2.4	9.0	4600
DC-56	TROC	26107	702.8	1.44	1.3	2.79	13	11.8	110	400	48	6.06	1910	5550	170	3.52	2.86	3.2	9.2	4500
DC-58	TROC	26107	682.5	2.00	1.4	3.08	10	15.9	160	710	140	8.79	2440	10200	113	0.71	2.65	4.6	6.6	4400
DC-61	TROC	26117	627.8	1.50	2.5	3.76	10	15.0	120	500	59	6.03	2050	7130	113	<3.8	0.56	4.3	7.5	3500
DC-79	TROC	26107	718.0	1.12	1.3	3.04	10	15.0	160	580	67	8.82	2250	7120	120	4.66	0.60	3.5	7.6	3200
DC-62	PGE	26107	627.5	1.69	3.5	10.5	34	65.6	560	2300	420	5.13	3740	12200	150	1.49	0.44	8.2	1.6	2100
DC-64	PGE	26117	609.2	0.59	4.1	8.62	31	47.6	300	1600	89	4.06	1680	3380	83	0.56	0.39	1.9	2.5	3100
DC-73	MS	26143	284.0	19.6	1.2	38.2	27	95.7	8.5	470	29	115	10700	12200	1100	40.5	0.37	25	8.4	7900
DC-75	MS	26117	716.5	31.2	3.8	2.28	<9.3	9.70	23	880	130	8.00	6840	11400	1240	387	0.84	13	16.0	24000
DC-76	MS	26143	328.9	34.9	4.6	27.1	40	96.0	35	1600	40	73	18700	5420	1050	102	2.58	43	12.0	8100
DC-65	CP	26143	288.2	2.17	<2.0	0.37	<5.0	2.37	370	600	270	0.79	1470	15700	109	14.8	1.38	8.2	11.0	2700
DC-67	CP	26143	229.0	3.42	<3.0	1.99	5.3	5.83	840	970	280	3.96	1570	14000	138	13.5	1.93	9.0	11.9	3800
DC-1	ARG	B2	135.9	0.02	<6	0.14	<5.0	0.17	3.1	1.8	5.4	0.07	67	39	39	7.16	1.83	<0.2	5.3	>1000
DC-3	ARG	B2	390.3	0.31	<9	0.07	<5.0	0.23	<3.2	2.4	<5.9	0.67	61	43	34	13.0	4.56	0.2	8.6	16000
DC-5	ARG	B2	464.8	0.53	<1.2	<0.7	<9.8	<3.7	6.5	4.9	2.8	0.68	89	73	26	25.8	5.09	<0.2	7.2	>27000
DC-7	ARG	B2	479.7	0.09	<6	0.04	<5.0	<3.1	<4.2	3.3	<1.6	0.34	48	46	32	8.96	2.47	<0.2	4.5	>4500
DC-8	ARG	B2	443.2	1.08	<7	0.10	<5.3	<2.0	3.5	2.6	<3.5	2.06	85	58	28	27.3	5.98	0.2	5.1	54000
DC-9	ARG	B2	245.3	0.03	<5	0.09	<5.0	0.13	3.9	<3.2	<1.6	0.20	78	59	35	3.83	1.83	<0.2	4.7	>1500
DC-70	BPU	outcrop	—	4.45	<1.5	0.06	<5.0	0.12	<4.7	3.5	<2.8	0.10	144	170	33	9.40	5.38	1.4	15.8	29000
			R.S.D. (%)	10	20	5	20	5	10	10	20	—	7	6	2	4	5	15	0.2 ¹	

NOTES: MS: massive sulfides; CP: chalcopyrite-rich sulfides; NOR: norite-hosted sulfides; TROC: troctolite-hosted sulfides; PGE: PGE-rich sulfides;

ARG: unmetamorphosed argillite of the Virginia Formation; BPU: bedded pyrrhotite unit of the Virginia Formation; $\delta^{34}\text{S}$: sulfur isotope values;

R.S.D.: Precision expressed as relative standard deviation (CANMET standards); ¹: precision at 2 σ error (IAEA-S1 and IAEA-S2 standards)

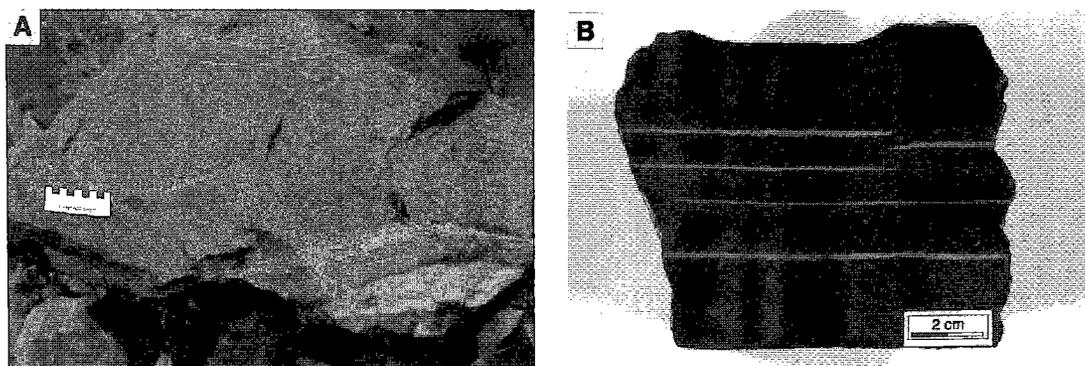


FIG. 3. A. Country-rock xenoliths hosted in heterogeneous norite and olivine gabbro near the base of the Dureka Pit deposit. Note the presence of granitic selvages along the margins of the xenoliths. B. Bedded pyrrhotite unit of the Virginia Formation showing thin laminations of pyrrhotite within hornfelsed argillite. Sample taken adjacent to the Dureka Pit deposit (DC-70, Tables 1, 2). Scale in centimeters for both photographs.

by a much thicker sequence dominantly consisting of leucotroctolite and olivine gabbro, with minor troctolite and norite.

In contrast to rocks of the upper cyclic units, which are generally well layered and contain very sparse sulfide, rocks of the basal part of the intrusion (lower 250 m) are mineralized and very heterogeneous in terms of texture and composition. Variations in grain size and modal mineralogy are considerable throughout this zone, and leucotroctolite, olivine gabbro and norite commonly occur together on a local scale.

Hornfels xenoliths derived from the underlying Virginia Formation comprise up to 25% of the volume of the basal sequence (Fig. 3A). Norite typically occurs in proximity of country-rock xenoliths or directly at the base of the intrusion. The norite was interpreted as having crystallized from a hybrid magma, produced through mixing between the parental basic magma and a granitic partial melt derived from the surrounding argillite (Thériault *et al.* 1997). Evidence of partial melting is indicated by the occurrence of granitic selvages along the margin of country-rock xenoliths (Fig. 3A). Furthermore, on the basis of trace-element geochemistry (Tyson & Chang 1984) and sulfur isotopes (Ripley 1981, Ripley & Alawi 1988), heat from the intrusion is interpreted to have led to the early transfer of a sulfur-bearing hydrous fluid from the footwall rocks into the basic magma. Hence, the highly heterogeneous and mineralized character of the basal rocks hosting the Dureka Road deposit appears to be related to a process of magma contamination through mixing with derivatives from the underlying Virginia Formation. An important contribution of sulfur seems to have come from what has been termed the bedded pyrrhotite unit (Severson & Hauck 1990), a 10- to 15-m-thick argillite horizon located approximately

25 m above the base of the Virginia Formation and containing 10–20% banded pyrrhotite (Fig. 3B). As shown from the drill-hole-interpreted cross-section of the deposit (Fig. 2), it is more than likely that this unit has been completely assimilated by the intruding magma on the basis of the reduced thickness (10–20 m) of the Virginia Formation in the Dureka Road area.

NATURE OF THE MINERALIZATION AT THE DUNKA ROAD DEPOSIT

The Dureka Road Cu-Ni-PGE sulfide deposit has estimated resources of 1450 million tonnes grading 0.397 wt.% Cu, 0.094 wt.% Ni, 445 ppb Pd, 118 ppb Pt, and 61 ppb Au (Wright Engineers Ltd. 1991).

The bulk of the mineralization (>95 vol.%) consists of disseminated sulfides, which comprise no more than 5 vol.% of the rock. The disseminated sulfides are typically interstitial to the silicates, and generally consist of pyrrhotite, chalcopyrite, pentlandite, and cubanite, with minor quantities of mackinawite, sphalerite, and bornite. Small amounts of the arsenides maucherite, niccolite, and cobaltite-gersdorffite, as well as the platinum-group mineral (PGM) froodite (PdBi_2), were observed locally with the sulfide minerals. Less than 5 vol.% of the mineralization consists of zones of massive sulfide dominated by pyrrhotite, with lesser pentlandite, chalcopyrite, cubanite, mackinawite, maucherite, and niccolite.

This study led to the identification of five types of sulfide mineralization within the Dureka Road deposit. These are: 1) norite-hosted disseminated sulfides, 2) troctolite-hosted disseminated sulfides, 3) PGE-rich disseminated sulfide horizons, 4) pyrrhotite-rich massive sulfides, and 5) chalcopyrite-rich disseminated sulfides surrounding lenses of massive sulfide.

Norite-hosted disseminated sulfides

The norite-hosted disseminated sulfides are typically found adjacent to country-rock xenoliths or within approximately 30 m of the basal contact of the intrusion. The mineralization consists mainly of pyrrhotite and ilmenite, with lesser chalcopyrite, cubanite, and pentlandite (Fig. 4A). Maucherite, niccolite and cobaltite–gersdorffite are also commonly observed, occurring as isolated grains enclosed within sulfides. This relationship suggests that the arsenides are primary magmatic phases crystallized from the sulfide liquid.

Troctolite-hosted disseminated sulfides

The troctolite-hosted disseminated sulfide mineralization occurs throughout the lower 250 m of the intrusion, and forms more than half of the deposit. The sulfides are mainly in leucotroctolite, distributed interstitially among the silicate minerals. They consist mainly of pyrrhotite, pentlandite, chalcopyrite, and cubanite, with trace amounts of mackinawite and bornite (Figs. 4B, C). The ratio of pyrrhotite to Cu- and Ni-rich sulfide phases is lower here than in the norite-hosted sulfides. Furthermore, only minor amounts of maucherite were observed.

PGE-rich disseminated sulfide horizons

Two horizons of disseminated sulfides distinctly enriched in the PGE, 10 m thick on average, were sampled from the upper portion of the mineralized zone. They occur 100 to 200 m above the basal contact (Fig. 2), and are hosted in leucotroctolite. The horizons typically underlie layers of melatroctolite to dunitite. They were first identified by Geerts (1991), who related their origin to a magmatic process rather than to secondary enrichment by a hydrothermal fluid.

The PGE-rich disseminated sulfide horizons contain up to 2.8 ppm Pt + Pd (Table 1), and consist mainly of interstitial grains of chalcopyrite, cubanite, pentlandite, and lesser pyrrhotite (Fig. 4D). Unlike the norite-

and troctolite-hosted sulfide mineralization, arsenide minerals were not observed in the PGE-rich horizons.

Pyrrhotite-rich massive sulfides

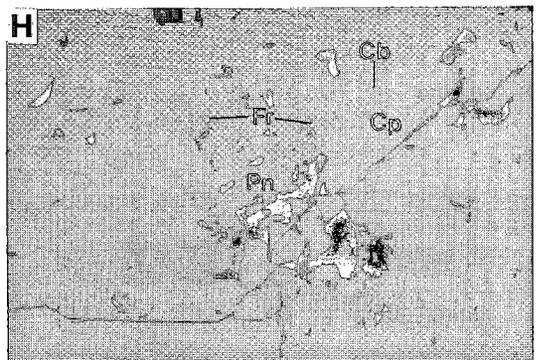
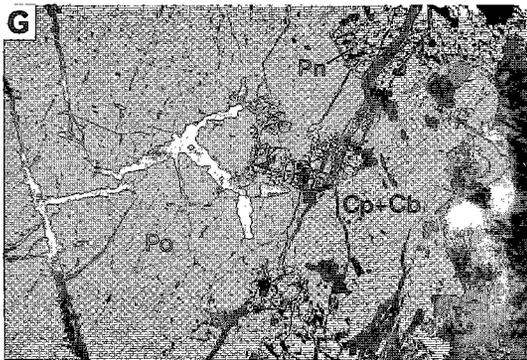
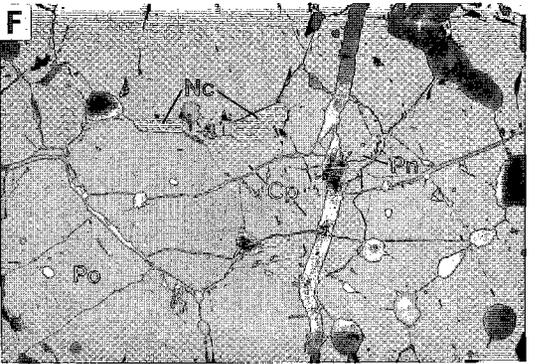
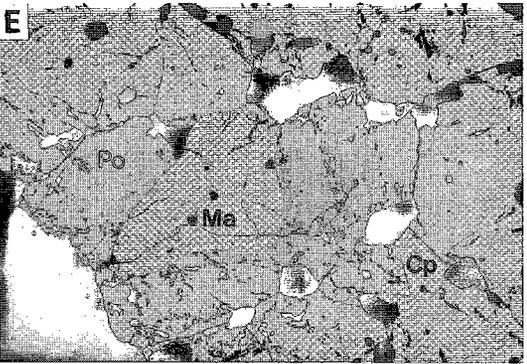
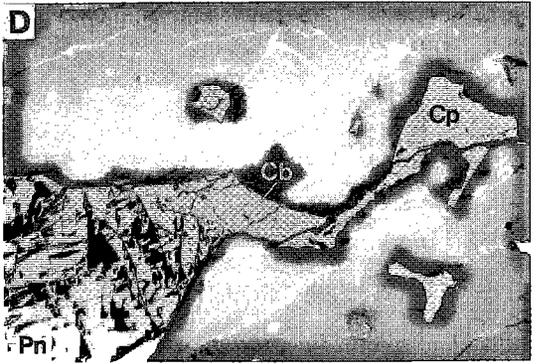
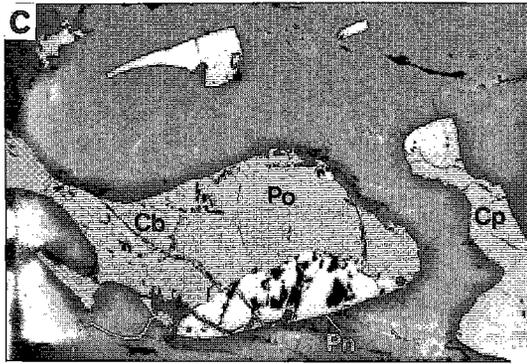
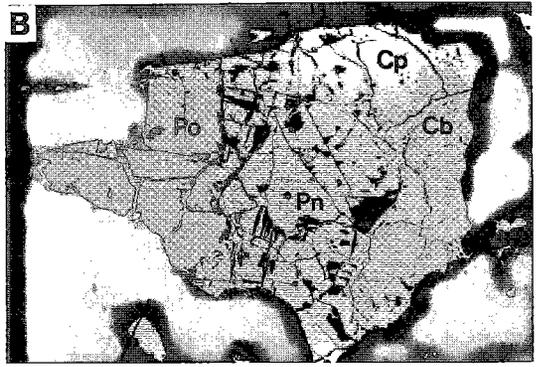
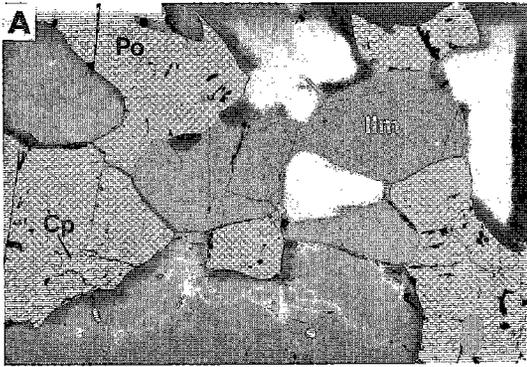
The pyrrhotite-rich massive sulfides occur as lenses in the basal sequence and, less commonly, as pods of massive sulfide bordering country-rock xenoliths. The massive sulfide pods (1–3 cm wide) are typically hosted in norite, and consist of 90–95% pyrrhotite, with minor chalcopyrite and pentlandite. They also contain maucherite and niccolite (Figs. 4E, F), and this is reflected in the elevated As content of sample DC-75 (Table 1). The massive sulfide pods and their noritic host are likely derived from *in situ* partial melting within the adjacent, sulfide-bearing country-rock xenoliths.

Several narrow lenses of massive sulfide reaching up to 5 cm in width occur in the basal mineralized rocks. They are usually at a sharp angle to the base of the intrusion, and are thus interpreted to originate as injections of sulfide liquid through a filter-pressing mechanism. The lenses contain 85–90% pyrrhotite, 5–10% pentlandite, and lesser chalcopyrite, cubanite and mackinawite. They are typically zoned, from a central core of massive pyrrhotite with minor flame-like pentlandite, to a narrow rim (1–2 mm) of subhedral pentlandite and marginal intergrowths of chalcopyrite, cubanite and minor mackinawite (Fig. 4G).

Chalcopyrite-rich disseminated sulfides

Chalcopyrite-rich disseminated sulfides are typically found in association with the pyrrhotite-rich lenses of massive sulfide. The disseminated sulfides occur as small interstitial grains to the silicate minerals or locally as very thin veinlets, and consist of 50–75% chalcopyrite, 15–30% pyrrhotite, 5–10% cubanite and 1–3% mackinawite, with minor sphalerite and bornite. Small subhedral grains of froodite surround pentlandite within a coarse-grained lamellar intergrowth of chalcopyrite and cubanite (Fig. 4H). The froodite appears to have nucleated on the pentlandite prior to the formation of the Cu-rich sulfide phases, which favors a

FIG. 4. A. Typical norite-hosted disseminated sulfide mineralization showing the close association of pyrrhotite (Po) and ilmenite (Ilm), with minor chalcopyrite (Cp) and cubanite (Cb). Field of view is 1.25 mm in width. B. Troctolite-hosted disseminated sulfide mineralization consisting of pyrrhotite (Po), pentlandite (Pn), chalcopyrite (Cp) and cubanite (Cb). Field of view is 1.25 mm in width. C. Troctolite-hosted mineralization illustrating the interstitial nature of the sulfides relative to the silicate minerals. Field of view is 1.25 mm in width. D. Interstitial sulfides from a PGE-rich horizon, consisting of pentlandite (Pn), cubanite (Cb) and chalcopyrite (Cp). Note the absence of pyrrhotite. Field of view is 1.25 mm in width. E. Grain of maucherite (Ma) with minor chalcopyrite (Cp) within a pyrrhotite-rich massive sulfide pod at the margin of a country-rock xenolith. Field of view is 1.25 mm in width. F. Subhedral crystals of niccolite (Nc) within the above pyrrhotite-rich massive sulfide pod. Pentlandite (Pn) and chalcopyrite (Cp) complete the sulfide assemblage. Field of view is 1.25 mm in width. G. Zoned massive sulfide lens consisting of a pyrrhotite-rich core, an inner rim of pentlandite (Pn) and a marginal intergrowth of chalcopyrite (Cp) and cubanite (Cb). Field of view is 5 mm in width. H. Subhedral crystals of froodite (Fr) at the margin of pentlandite (Pn), within Cu-rich disseminated sulfides composed of intergrown chalcopyrite (Cp) and cubanite (Cb). Field of view is 0.3 mm in width.



magmatic origin for the PGM, as opposed to its crystallization from a late hydrothermal fluid.

SULFUR ISOTOPES

Sulfur isotope studies carried out on several Cu–Ni sulfide deposits of the Duluth Complex indicate that most of the sulfur has been derived from argillaceous rocks of the underlying Virginia Formation (Mainwaring & Naldrett 1977, Ripley 1981, 1986, Ripley & Al-Jassar 1987). Ripley (1981) obtained $\delta^{34}\text{S}$ values ranging from 0.2 to 15.3‰ from mineralized intrusive rocks of the Dunka Road deposit, values that cover a range similar to those values he measured in the Virginia Formation.

Virginia Formation

Sulfur isotope measurements were obtained from six core samples of unmetamorphosed pyritiferous argillite taken approximately 20 km from the intrusive contact (drill hole #B2, Fig. 1). The samples are considered representative of the unit, having been collected between 3 and 345 m above the basal contact with the Biwabik Formation. Values of $\delta^{34}\text{S}$ range from 4.5 to 8.6‰ (Table 1, Fig. 5), and are similar to the value of 7.4‰ determined by Ripley (1981) on material from the same drill hole, and to the range of results of six analyses reported by Ripley & Al-Jassar (1987) (5.6 to 8.8‰) from core samples located 10 km from the margin of the Complex.

One sample of metamorphosed argillite from the bedded pyrrhotite unit (DC-70; Table 1, Fig. 5) yielded a much higher value, 15.8‰, and falls within the range of $\delta^{34}\text{S}$ values determined by Severson (1994) (14.0 to 21.1‰). Sulfur isotope measurements of the same unit were also obtained by Zanko *et al.* (1994) from a 17-m-thick xenolith occurring along the base of the Serpentine deposit. The $\delta^{34}\text{S}$ values show a systematic increase from 6.3 to 29.1‰ (mean of 19.4‰) toward the top of the xenolith (their Fig. 10). This increase is associated with an upward increase in the grade of metamorphism; reported mineral assemblages and textures are indicative of complete dehydration and localized partial melting near the top, whereas relict chlorite and muscovite found at the base indicate that dehydration reactions did not go to completion. Similar variations in $\delta^{34}\text{S}$ values with proximity to the intrusive contact have also been reported from the Muskox Intrusion (Sasaki 1969) and the Pechenga ore field in Russia (Melezhik *et al.* 1994). Hence the strong positive correlation observed between $\delta^{34}\text{S}$ values of the argillaceous rocks and grade of metamorphism makes it improbable that the isotopic variability in the Virginia Formation is related to a primary process of bacterial fractionation, as was suggested by Zanko *et al.* (1994).

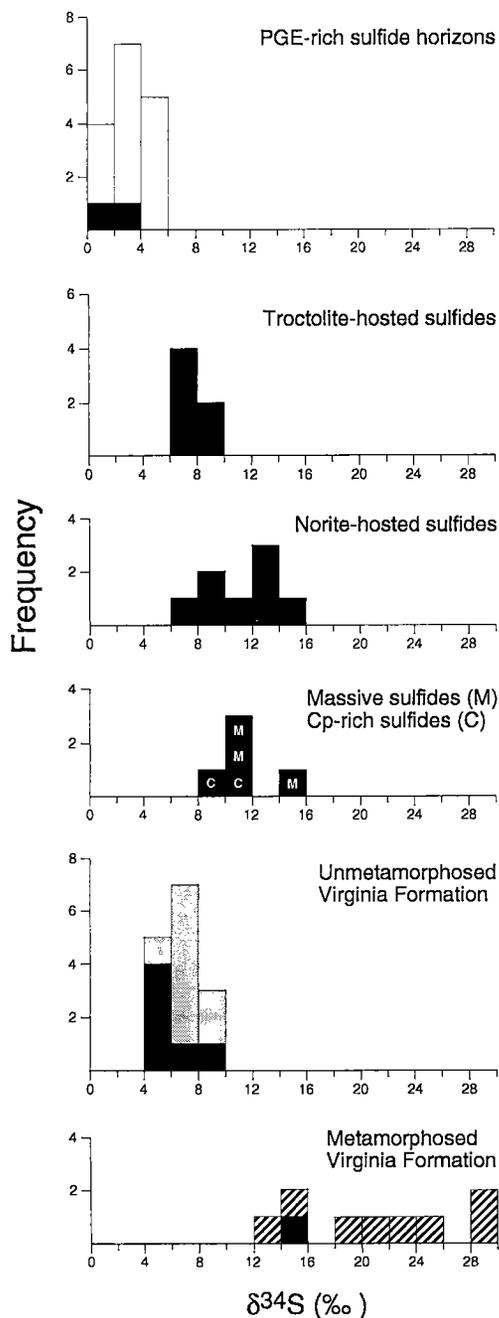


FIG. 5. Histogram showing the distribution of sulfur isotopic values for the five types of sulfide mineralization forming the Dunka Road deposit, as well as the bedded pyrrhotite unit and unmetamorphosed argillite of the Virginia Formation. Black boxes: this study; white boxes: Geerts (1994); grey boxes: Ripley (1981), Ripley & Al-Jassar (1987), Zanko *et al.* (1994); striped boxes: Severson (1994), Zanko *et al.* (1994).

As proposed by Zheng (1990) for an open system, we argue that the significantly higher $\delta^{34}\text{S}$ values observed in metamorphosed argillaceous rocks near the contact originate from the breakdown of pyrite into pyrrhotite under hydrous conditions, with release of a light-sulfur-enriched vapor into the magma prior to the onset of crystallization. Such a process has previously been demonstrated experimentally by Kajiwara *et al.* (1981) through the thermal decomposition of pyrite into pyrrhotite at 600°C. They observed a significant depletion in $\delta^{34}\text{S}$, by up to 12‰, in the early fraction of sulfur released, with the pyrrhotite residue having a $\delta^{34}\text{S}$ value about 4.5‰ higher than the starting material. Hence the early release of a light-sulfur-enriched vapor phase into the magma most likely led to a significant increase in the $\delta^{34}\text{S}$ of the residual pyrrhotite-bearing metasedimentary rocks, the later subsequently discharging important quantities of isotopically heavier sulfur near the base of the intrusion during their partial assimilation.

Norite-hosted, troctolite-hosted and PGE-rich disseminated sulfides

Sulfur isotope measurements obtained from these three types of disseminated sulfide mineralization show a general increase in $\delta^{34}\text{S}$ toward the base of the intrusion and in proximity to country-rock xenoliths (*i.e.*, where magma contamination is likely to be most important). Hence the average $\delta^{34}\text{S}$ value of the norite-hosted sulfides reaches 11.2‰, whereas that of the troctolite-hosted and PGE-rich sulfides is 7.8 and 2.1‰, respectively, with only a slight overlap between the groups of values (Table 1, Fig. 5). A similar variation with respect to distance from the basal contact was noted by Ripley (1981) based on 128 sulfur isotope analyses from the mineralized intrusive rocks. Of these, 14 samples from the uppermost PGE-rich horizon (the "Red Horizon" of Geerts 1994) yielded an average $\delta^{34}\text{S}$ value of 3.6‰ (Fig. 5), which is comparable to that of the present study.

Pyrrhotite-rich massive and chalcopyrite-rich disseminated sulfides

Sulfur isotope measurements obtained from the pyrrhotite-rich and chalcopyrite-rich sulfides yielded relatively high $\delta^{34}\text{S}$ values, ranging from 8.4 to 16.0‰ (Table 1), which suggest that a large proportion of the sulfur is sedimentary in origin. The very high value obtained for the massive sulfide pod (sample DC-75, 16.0‰) is almost identical to that measured for the bedded pyrrhotite unit. This is not surprising, as DC-75 was sampled directly adjacent to a country-rock xenolith. As for the pyrrhotite-rich lenses and associated chalcopyrite-rich disseminated sulfides, the very similar values obtained within each pair of samples imply that little to no isotopic fractionation

occurred during their formation. A similar conclusion was reached by Ripley & Al-Jassar (1987) on the basis of $\delta^{34}\text{S}$ values of mineral separates from adjacent pyrrhotite and cubanite within the Babbitt deposit.

S/Se VALUES

The ratio Se/S has been used effectively to determine the source of sulfur in magmatic Ni-Cu sulfide deposits (*e.g.*, Paktunc 1989, Eckstrand *et al.* 1989, Ripley 1990a, Thériault *et al.* 1997). Its usefulness is particularly significant where country-rock assimilation seems to have played a role in the genesis of mineralization, as sedimentary rocks are generally depleted in selenium relative to mantle-derived rocks (Eckstrand & Hulbert 1987).

Norite-hosted, troctolite-hosted and PGE-rich disseminated sulfides

Our data show that whole-rock S/Se values decrease systematically from the norite-hosted sulfides (mean of 9,700) to the troctolite-hosted sulfides (mean of 4,600), and reach a minimum in the PGE-rich sulfide horizons (mean of 2,600) (Table 1). In light of the elevated S/Se values of the argillite samples from the Virginia Formation, which range from 15,500 to 54,000, we attribute this regular decrease in S/Se to varying degrees of its assimilation by the mafic magma. Similar S/Se values (mean of 23,300) were also obtained in the district by Eckstrand & Cogulu (1986) from argillaceous rocks of the equivalent Rove Formation in proximity to the Ni-Cu sulfide deposit in the Crystal Lake Gabbro.

Pyrrhotite-rich massive and chalcopyrite-rich disseminated sulfides

The pyrrhotite-rich massive sulfides have significantly higher S/Se values than the chalcopyrite-rich disseminated sulfides (Table 1). The high value obtained for the massive sulfide pod (sample DC-75: 23,800) falls within the range for the argillaceous rocks; this is in agreement with its very high $\delta^{34}\text{S}$ value and points to a significant input of metasediment-derived sulfur.

DISCUSSION

Country-rock assimilation

A number of lines of evidence presented above strongly support the assumption that country-rock assimilation was a key process in the genesis of the Dunka Road Cu-Ni-PGE deposit. With respect to field observations, the abundance of hornfels xenoliths typically rimmed by granitic material, along with the common presence of norite near the base of the mineralized intrusion, are indicative of significant

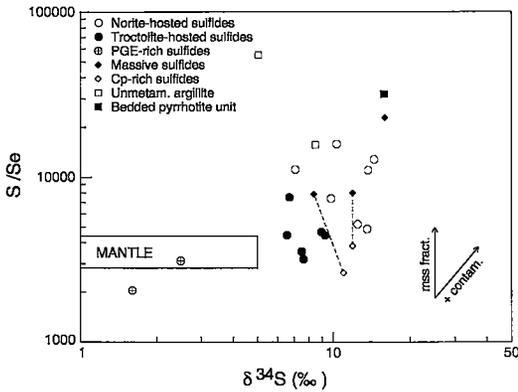


FIG. 6. Whole-rock S/Se ratio versus $\delta^{34}\text{S}$ value for the five types of sulfide mineralization, bedded pyrrhotite unit and unmetamorphosed argillite of the Virginia Formation. Range in S/Se ratio and $\delta^{34}\text{S}$ value of the mantle taken from Eckstrand & Hulbert (1987) and Hulbert *et al.* (1988), respectively.

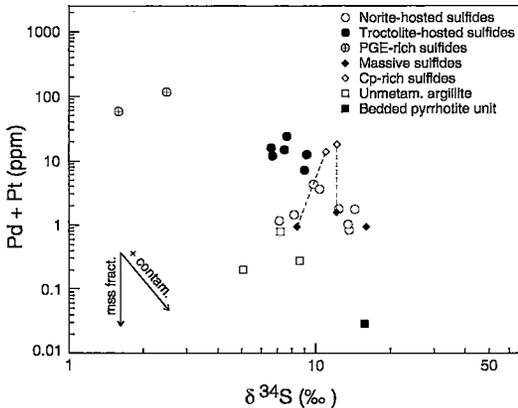


FIG. 7. Whole-rock $\delta^{34}\text{S}$ value versus Pd + Pt of sulfide fraction for the five types of sulfide mineralization, bedded pyrrhotite unit and unmetamorphosed argillite of the Virginia Formation. Broken lines join samples of pyrrhotite-rich massive sulfide lenses and associated chalcopyrite-rich disseminated sulfides. Arrows show compositional trend expected during *mss* fractionation and magma contamination. Symbols are the same as in Figure 6.

contamination of the parental magma through partial melting of the underlying Virginia Formation. There is also an apparent relationship between the relative abundances of pyrrhotite and arsenide minerals and the extent of contamination, owing to the Cu–Ni-poor and As-rich composition of the argillaceous country-rocks relative to the parental mafic magma.

Furthermore, sulfur isotope measurements and S/Se values of the mineralized rocks clearly demonstrate that

a significant proportion of the sulfur is sedimentary in origin, being most likely derived in large part from the bedded pyrrhotite unit of the Virginia Formation. The wide range in $\delta^{34}\text{S}$ values of the mineralized intrusive rocks is consistent with a simple mixing model between “igneous” sulfur contained in the magma ($\delta^{34}\text{S} \approx 0\text{‰}$) and externally derived sedimentary sulfur represented by the bedded pyrrhotite unit ($\delta^{34}\text{S} \approx 15.8\text{‰}$). The assumed $\delta^{34}\text{S}$ value for magmatic sulfur is supported by recent isotopic measurements obtained by Lee & Ripley (1995) for 12 unmineralized samples of troctolite from the South Kawishiwi intrusion, which yielded values ranging from -3.4 to $+1.2\text{‰}$ (mean of $+0.1\text{‰}$). Assuming the two end members to be valid,

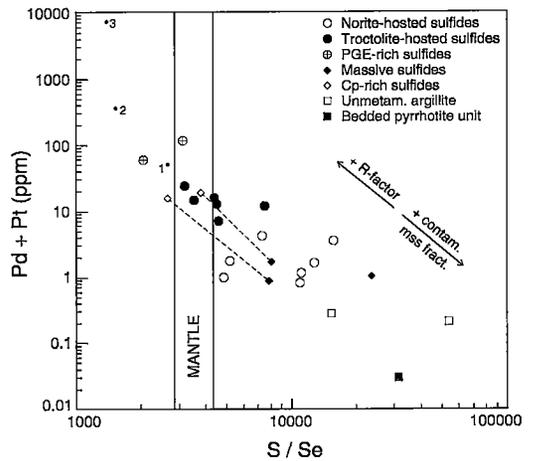


FIG. 8. Whole-rock S/Se ratio versus Pd + Pt of sulfide fraction for the five types of sulfide mineralization forming the Dunka Road deposit, bedded pyrrhotite unit and unmetamorphosed argillite of the Virginia Formation, and various PGE-dominant magmatic sulfide deposits (1: Crystal Lake gabbro, 2: Merensky Reef of the Bushveld Complex, 3: J-M Reef of the Stillwater intrusion). Data for other deposits taken from Naldrett (1981) and Eckstrand (unpubl. data, 1988). Symbols are the same as in Figure 6.

an average of 71% of the sulfur within the norite-hosted sulfides seems to have been derived from the footwall rocks, as opposed to 49% for the troctolite-hosted sulfides and only 13% for the PGE-rich sulfides.

The observed increase in $\delta^{34}\text{S}$ values with degree of country-rock assimilation is associated with a concomitant increase in S/Se values (Fig. 6), as well as a decrease in the Pd + Pt content of the sulfide fraction (Fig. 7). The latter is also suggestive of a mixing process between PGE-poor partial melts of the Virginia Formation and metal-bearing mafic magmas. Lower *R* factors (*i.e.*, weight ratio of silicate magma to sulfide

melt) attained in the more contaminated rocks also contribute to this gradual decrease in PGE (Thériault *et al.* 1997). Moreover, a plot of S/Se values *versus* Pd + Pt content of the sulfide fraction (Fig. 8) clearly illustrates the contaminated nature of the norite-hosted sulfides, which have S/Se values above those estimated for mantle-derived rocks (2850–4350; Eckstrand & Hulbert 1987). The low S/Se value and high Pd + Pt content of the PGE-rich sulfide horizons have been ascribed in part to elevated *R* factors achieved at the time of separation of the sulfide liquid (Thériault *et al.* 1997). These values are not unlike those of major PGE-rich deposits (Fig. 8), whose origin also has been linked to very large *R* factors (Campbell *et al.* 1983). As for the spatially associated pyrrhotite-rich and chalcopyrite-rich sulfide samples, the difference in S/Se values and Pd + Pt content likely relates to a difference in the extent of sulfide liquid fractionation, considering that both samples within a pair seem to have undergone comparable degrees of assimilation based on their similar $\delta^{34}\text{S}$ values (Table 1).

Additional geochemical evidence (Thériault *et al.* 1997) further confirm the importance of the assimilation process. For example, electron-microprobe analyses of the sulfide phases suggest a higher proportion of monoclinic to hexagonal pyrrhotite in the norite-hosted sulfides, which was interpreted to be due to the greater availability of locally derived sulfur from the metasedimentary country-rocks. Moreover, an increase in the incompatible elements such as Cs, Rb, Ba and Th was noted in the more contaminated samples, as one would expect these elements to be readily mobilized in a felsic partial melt.

Magmatic origin of the sulfides

A number of studies pertaining to the Babbitt deposit have emphasized the role of hydrothermal fluids in remobilizing the PGE (*e.g.*, Ripley 1990b, Mogessie *et al.* 1991, Mogessie & Stumpfl 1992, Ripley *et al.* 1993, Ripley & Chryssoulis 1994), on the basis of the common presence of platinum-group minerals (PGM) and secondary sulfides (bornite, vallerite and violarite) in strongly altered silicate rocks. However, studies carried out in the Dunka Road deposit report only minor evidence of hydrothermal alteration, and relate the origin of mineralization to primary magmatic processes (*e.g.*, Ripley 1981, Rao & Ripley 1983, Severson & Hauck 1990, Geerts 1994, Thériault *et al.* 1997). In the present study, field and petrographic evidence suggest that the bulk of the mineralization (norite-hosted, troctolite-hosted, and PGE-rich sulfides) formed by the separation of sulfide liquid within a partially crystallized magma, which may explain the general lack of massive sulfides along the base of the intrusion. Where a relatively large volume of sulfide liquid did accumulate, it appears to have undergone fractional crystallization, producing an

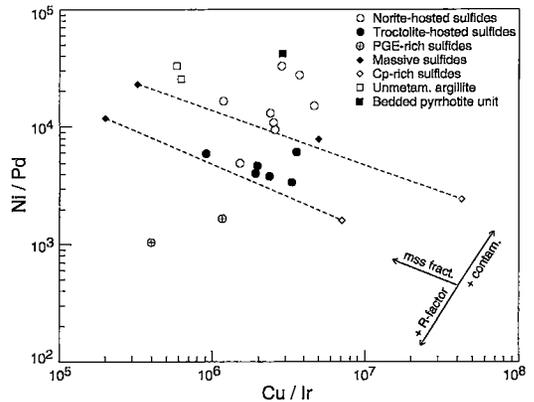


FIG. 9. Cu/Ir *versus* Ni/Pd diagram for the five types of sulfide mineralization, bedded pyrrhotite unit and unmetamorphosed argillite of the Virginia Formation. Symbols are the same as in Figure 6.

Fe-rich cumulate of monosulfide solid-solution (*mss*) and a Cu-rich fractionated sulfide liquid.

On a plot of Cu/Ir *versus* Ni/Pd (Fig. 9), two distinct features can be recognized: 1) a gradual decrease in Ni/Pd and Cu/Ir values from the norite-hosted to the troctolite-hosted sulfides, reaching a minimum in the PGE-rich sulfide horizons, and 2) a decrease in Ni/Pd ratio with concomitant increase in Cu/Ir ratio from the massive sulfide lenses to their associated chalcopyrite-rich disseminated sulfides. In the first case, the systematic decrease in metal ratios is due to an increase in the PGE content of the sulfides, brought about by a rise in the *R* factor as the effect of country-rock assimilation diminishes away from the basal contact. This relationship was recently demonstrated by Thériault *et al.* (1997), who modeled the composition of the above three types of disseminated sulfide mineralization using the equation for equilibrium fractionation, and obtained average *R* factors of 175, 1300 and 8000 for the norite-hosted, troctolite-hosted and PGE-rich sulfides, respectively. A similar increase in PGE content (hence *R* factor) with distance away from the intrusive margins was also observed by Barnes & Francis (1995) in the Muskox intrusion, in the Northwest Territories. As for the associated massive sulfide lenses and chalcopyrite-rich sulfides, we explain the observed variation in metal ratios by the fractionation of Ir and, to a lesser extent, of Ni into *mss*, with Cu and Pd behaving as incompatible elements and being concentrated in the residual sulfide liquid. The metal ratio of the massive sulfide pod sample (DC-75) in proximity to the field of norite-hosted sulfides suggests that it has not undergone significant fractional crystallization, which is substantiated by the apparent lack of chalcopyrite-rich sulfides in the immediate area.

The whole-rock metal content of all mineralized samples was recalculated to 100% sulfides for the purpose of comparing the composition of the sulfide fraction of each type of mineralization (Table 2). The normative composition of the sulfide fraction was then calculated. Results clearly support the petrographic observations, and show that the proportion of base-metal sulfides (*i.e.*, chalcopyrite, cubanite, and pentlandite) increases relative to pyrrhotite as the effect of country-rock assimilation wanes away from the basal contact. Furthermore, a striking increase in the normative proportion of Cu-rich sulfides is observed within the disseminated mineralization surrounding massive pyrrhotite-rich lenses, as predicted by the fractional crystallization model.

TABLE 2. AVERAGE METAL CONCENTRATIONS AND NORMATIVE MINERALOGY OF THE SULFIDE FRACTION

Rock type	NOR	TROC	PGE	MS ¹	CP	ARG ²
S (%)	36.1	35.7	35.2	36.3	35.5	36.4
Fe (%)	57.9	45.1	33.9	60.2	42.7	63.2
Cu (%)	4.45	15.3	22.5	1.39	19.9	0.08
Ni (%)	1.26	3.77	8.14	1.93	1.75	0.08
Os (ppb)	14	40	160	3	14	<55
Ir (ppb)	20	80	370	49	13	4
Ru (ppb)	170	280	1300	46	48	<370
Rh (ppb)	58	310	2100	140	50	11
Pt (ppb)	470	2900	15000	26	7400	190
Pd (ppb)	1500	11000	72000	1300	10000	180
Au (ppb)	330	1700	7000	47	3600	88
Re (ppb)	82	160	180	140	27	49
Co (ppm)	2300	1700	2000	1500	900	1200
As (ppm)	280	140	32	90	190	1100
Sb (ppm)	66	74	16	2	21	280
Se (ppm)	41	83	140	46	110	12
Cp+Cb (%)	13	44	64	4	57	0
Pn (%)	4	12	26	6	6	0
Pa (%)	83	44	10	90	37	100

NOTES: Composition of the sulfide fraction calculated allowing 200 ppm Ni and 150 ppm Cu in the silicate component of the intrusive rocks. Details of the calculations in Barnes & Francis (1995). ¹: includes only massive sulfide lenses (*i.e.* DC-73 and DC-76); ²: includes both argillite and bedded pyrrhotite unit.

The recalculated composition of the sulfide fraction of each type of mineralization was plotted on mantle-normalized variation diagrams to better compare their level of metal enrichment. As shown in Figure 10A, the PGE-rich sulfides are strongly enriched in metals relative to the troctolite-hosted and norite-hosted sulfides, particularly in PGE and Au. In contrast, the sample from the bedded pyrrhotite unit shows a strong depletion in all metals, and plots closest to the field of norite-hosted sulfides. The following enrichment-factors were calculated between the average PGE-rich and norite-hosted sulfides: Cu(5), Ni(6), Os(11), Ru(16),

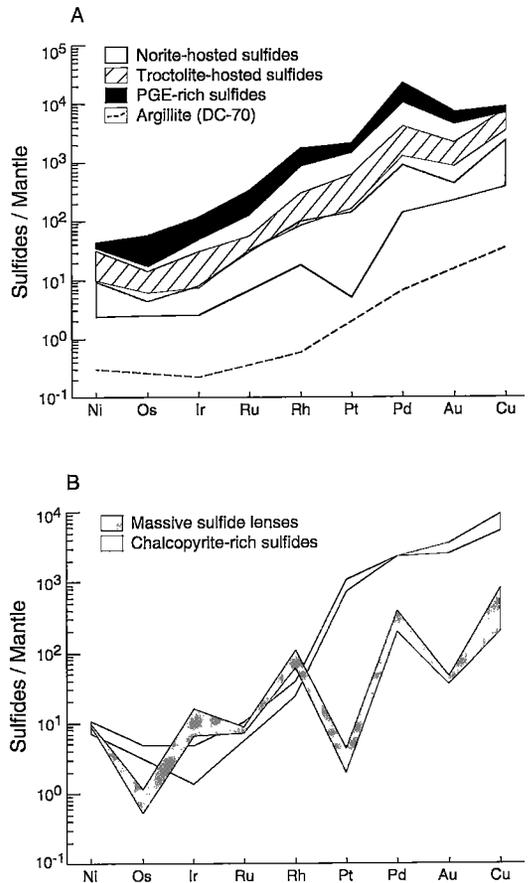


FIG. 10. Mantle-normalized metal patterns showing the range in composition of the sulfide fraction. A. Norite-hosted, troctolite-hosted and PGE-rich disseminated sulfides, and the bedded pyrrhotite unit of the Virginia Formation. B. Lenses of pyrrhotite-rich massive sulfide and associated chalcopyrite-rich disseminated sulfides. Normalization factors are from Barnes *et al.* (1988).

Ir(18), Au(21), Pt(31), Rh(36), and Pd(49). The higher enrichment-factors of the Pd-group of PGE (Rh, Pt, and Pd; Barnes *et al.* 1985) possibly relates to their higher partition-coefficient into the sulfide liquid. The gradual increase in metal content observed from the norite-hosted to the PGE-rich sulfides probably reflects a number of factors, including the degree of country-rock assimilation, the ratio of silicate melt to sulfide liquid, and the partition coefficient of metals into the sulfide liquid.

The mantle-normalized patterns of the massive sulfide lenses and associated chalcopyrite-rich dissemi-

nated sulfides show a clear antithetic relationship (Fig. 10B), with the former having higher contents in Ir, Ru and Rh, whereas the chalcopyrite-rich sulfides are strongly enriched in the more incompatible metals (*i.e.*, Pt, Pd, Au and Cu). A striking characteristic of the massive sulfides is their strong negative anomalies in Pt and Au relative to the smoother pattern of the chalcopyrite-rich assemblages. Similar patterns have also been described from sulfides of the Noril'sk-Talnakh District (Zientek *et al.* 1994, Barnes *et al.* 1997a), the Cape Smith Fold Belt (Barnes *et al.* 1997a) and the Stillwater Complex (Zientek *et al.* 1994), and illustrate the highly variable partitioning of metals between *mss* and the sulfide liquid.

To assess the degree of compatibility of metals in *mss*, the recalculated composition of each lens of pyrrhotite-rich massive sulfide was divided by that of its associated chalcopyrite-rich zone of disseminated sulfide mineralization (Fig. 11). Results show that Re, Ir and Rh appear to partition strongly into *mss*, whereas Pd, Sb, Cu, Au and Pt are highly incompatible and show an increasing affinity for the sulfide liquid. The average ratio of concentration in pyrrhotite-rich assemblage to that in chalcopyrite-rich assemblage was calculated for each metal, and yielded: Re(5.3), Ir(3.8), Rh(2.8), Co(1.6), Ni(1.1), Ru(0.96), As(0.47), Se(0.40), Pd(0.13), Sb(0.10), Cu(0.07), Au(0.01) and Pt (0.004). These values are quite similar to those obtained for other deposits (*e.g.*, Zientek *et al.* 1994, Li & Barnes 1996), and compare favorably with experimentally determined partition-coefficients (*e.g.* Fleet *et al.* 1993, Li *et al.* 1996, Barnes *et al.* 1997b), considering that the lenses of massive sulfide are not perfect *mss* accumulates (*i.e.*, they contain some fractionated liquid component, manifested as a narrow Cu-rich rim). The apparently incompatible nature of Se with respect to *mss* could explain the lower S/Se of the chalcopyrite-rich sulfides relative to the lenses of massive sulfide (Table 1, Figs. 6, 8).

Genesis of the Dunka Road deposit

The origin of the Dunka Road Cu-Ni-PGE deposit has been interpreted in terms of three main processes, which operated in sequence. Each of the five types of sulfide mineralization may be explained by the combined action of an externally derived process, country-rock assimilation, and two internal magmatic processes, namely the interaction between the sulfide liquid and the silicate melt, and fractional crystallization of the sulfide liquid. In light of the above, we interpret the sequence of events as follows (Fig. 12):

1) Early during emplacement of the Partridge River intrusion, the surrounding sedimentary rocks were contact-metamorphosed, leading to their partial dehydration and devolatilization. A light-sulfur-enriched H₂S vapor phase was released into the magma

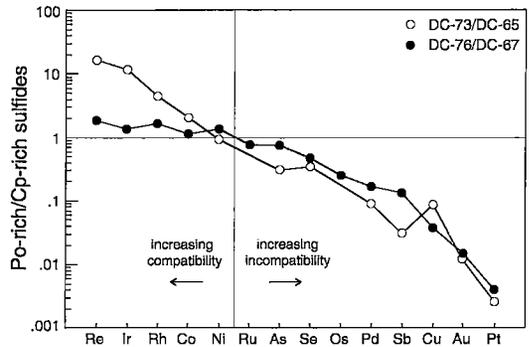
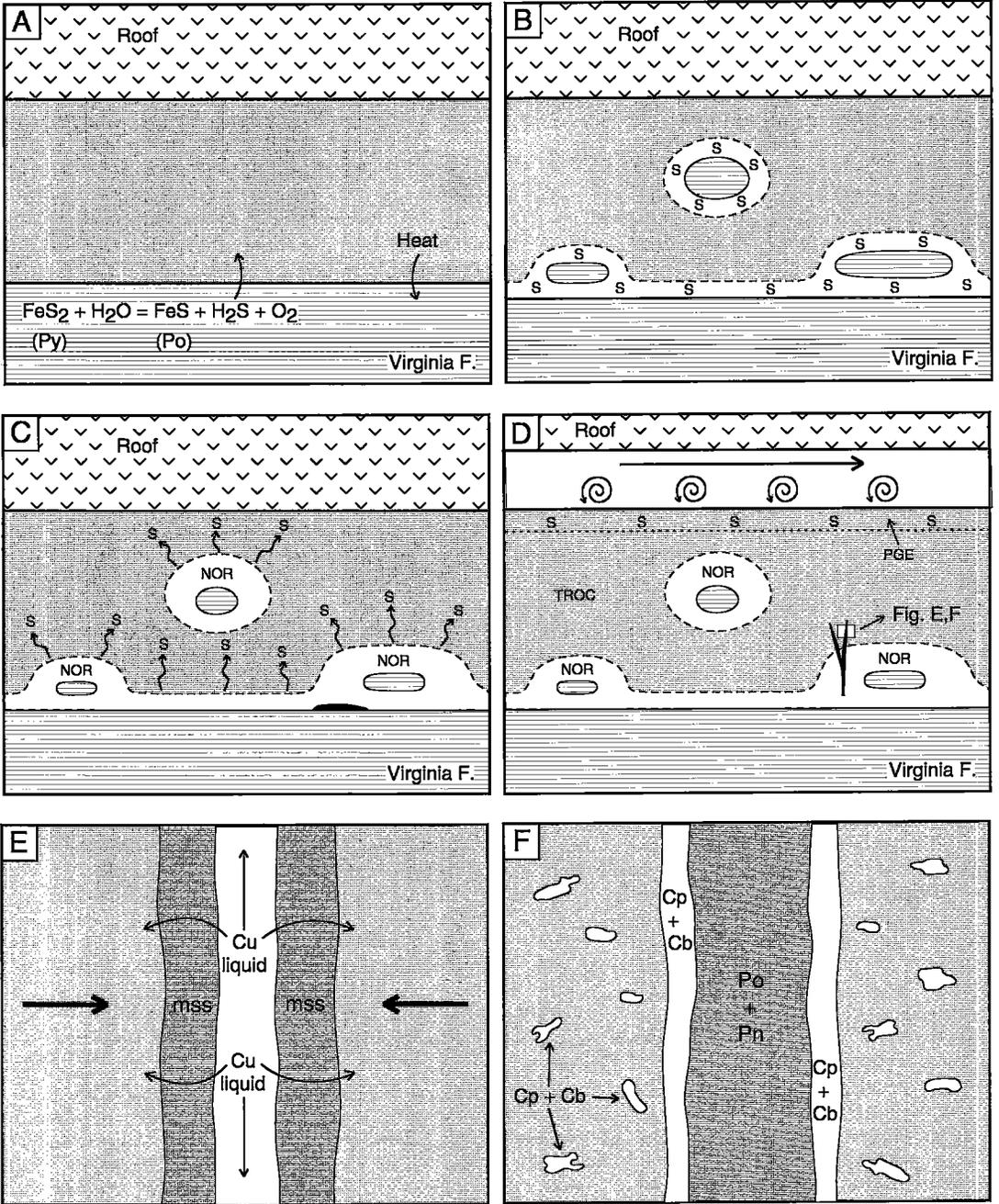


FIG. 11. Variation diagram showing the degree of compatibility of metals in the pyrrhotite-rich massive sulfide lenses relative to their associated chalcopyrite-rich disseminated sulfide mineralization.

through the breakdown of pyrite into pyrrhotite, and either homogenized with the resident juvenile sulfur or escaped to surface *via* overlying flows of flood basalt (Fig. 12A).

2) The restitic, light-sulfur-depleted pyrrhotite-bearing metasedimentary rocks were subsequently assimilated by the magma, releasing a granitic partial melt and important quantities of ³⁴S-enriched sulfur near the base of the intrusion and in proximity to country-rock xenoliths. Owing to intense contamination by the granitic melt, the hybridized noritic magma was cooler than the surrounding troctolitic magma, which led to its early crystallization and formation of the norite-hosted disseminated sulfide mineralization (Fig. 12B). The sulfide liquid crystallized near its source and had less time to interact with the magma, resulting in low *R* factors. This hypothesis explains the metal-poor and pyrrhotite-rich nature of the norite-hosted sulfides. Furthermore, the sulfide liquid was As-rich and Se-poor owing to the large contribution of sedimentary material to the magma, which is shown by the relative abundance of arsenide minerals and elevated S/Se values.

3) A significant proportion of ³⁴S-enriched sulfur also diffused into the surrounding troctolitic magma, mixing with juvenile igneous sulfur (Fig. 12C). The less contaminated and thus hotter troctolitic magma had longer to cool than the noritic magma. Therefore, the sulfide liquid had longer to interact with the silicate melt, which led to higher *R* factors. This finding explains the significant increase in the PGE content of the troctolite-hosted disseminated sulfides.



4) A fresh input of relatively uncontaminated troctolitic magma was later injected above the basal mineralized sequence. The low volume of sulfide liquid present near the base of this new injection was free to swirl within the turbulent magma, achieving very elevated R factors. Eventually, this ^{34}S -depleted sulfide liquid percolated downward into the partly consolidated troctolitic rocks, and crystallized to form a PGE-rich disseminated sulfide horizon (Fig. 12D). As these sulfides were largely derived from a mafic magma, they have low As concentrations and S/Se values close to those typical of the mantle.

5) In areas where significant amounts of sulfide liquid collected (*e.g.*, likely along the base, in proximity to the bedded pyrrhotite unit), it was filter-pressed upward to accumulate as subvertical injections (Fig. 12D). The sulfide liquid subsequently underwent fractional crystallization, forming an Fe-rich cumulate of *mss* that crystallized along the cooler margin of the lenses. The residual Cu-rich sulfide liquid, which would have accumulated within the central part of the lenses, was eventually expelled along the outer margin of the lenses as well as into the surrounding mush of crystals (Fig. 12E). This fractionated sulfide liquid ultimately crystallized as chalcopyrite and cubanite along the outer margin of the lenses, as well as within the adjacent intrusive rocks, to form the chalcopyrite-rich disseminated sulfide mineralization. With further cooling, the *mss* exsolved into pyrrhotite and pentlandite, forming the inner part of the observed lenses of massive sulfide (Fig. 12F).

Post-crystallization hydrothermal remobilization of the metals appears to have been minimal, on the basis of the lack of significant alteration throughout the deposit.

CONCLUSIONS

Compositional variations in magmatic sulfides of the Dunka Road Cu-Ni-PGE deposit are best explained by varying degrees of country-rock assimilation, which in turn affected the amount of interaction between the sulfide liquid and the silicate melt (R factor). Fractional crystallization of sulfide liquid subsequently occurred within localized lenses of massive sulfide.

In this study, we have confirmed the significant role of country-rock assimilation in localizing the mineralization; this aspect had been emphasized in previous studies (*e.g.*, Ripley 1981, Rao & Ripley 1983, Geerts 1991). In addition, however, we have been able to monitor systematic variations in the intensity of the process through detailed field, petrographic, geochemical and isotopic studies of the mineralization.

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FIG. 12. Schematic diagram illustrating the processes involved in the formation of the five types of sulfide mineralization from the Dunka Road deposit. The figure is not meant to be to scale. A. Early during contact metamorphism, a light-sulfur-enriched H_2S vapor phase is released into the troctolitic magma through the breakdown of pyrite to give pyrrhotite. B. The restitic, light-sulfur-depleted metasedimentary rocks are later assimilated by the magma, releasing a granitic partial melt and important quantities of ^{34}S -enriched sulfur near the base of the intrusion and in proximity to country-rock xenoliths. The hybridized magma and metal-poor sulfide liquid eventually crystallize, forming the norite-hosted disseminated sulfide mineralization. C. A significant proportion of ^{34}S enriched sulfur also diffuses into the surrounding troctolitic magma, mixing with juvenile igneous sulfur. The immiscible sulfide liquid interacts with a larger volume of silicate magma, and crystallizes to form troctolite-hosted disseminated sulfides having moderate PGE contents. D. A fresh input of uncontaminated troctolitic magma is injected above the basal mineralized unit. Sulfide liquid from this new injection is free to swirl within the turbulent magma, and eventually percolates downward into the partly consolidated rocks to form a PGE-rich disseminated sulfide horizon. Meanwhile, small pools of sulfide liquid near the base of the intrusion are filter-pressed upward to form subvertical injections. E. The sulfide liquid undergoes fractional crystallization, forming a cumulate of *mss* that crystallizes along the lens margins. Residual Cu-rich sulfide liquid accumulates in the central part of the lens, and is eventually expelled along the outer margins as well as into the surrounding crystal mush. F. With further cooling, the fractionated sulfide liquid crystallizes into chalcopyrite and cubanite while the *mss* exsolves into pyrrhotite and pentlandite, forming the observed pyrrhotite-rich massive sulfide lenses and associated chalcopyrite-rich disseminated sulfide mineralization.

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