

MINNESOTA GEOLOGICAL SURVEY

MATT S. WALTON, *Director*

**GEOLOGY OF THE
DEER LAKE COMPLEX,
ITASCA COUNTY, MINNESOTA**

**Cumulus Mineralogy and Petrology of the
Deer Lake Complex, Itasca County, Minnesota**

John L. Berkley and Glen R. Himmelberg

**Sulfide Minerals in the Layered Sills of the
Deer Lake Complex, Itasca County, Minnesota**

Edward M. Ripley



Report of Investigations 20-A, B

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PREFACE

This report describes the geology, petrology, and sulfide mineralogy of differentiated peridotite-gabbro sills that crop out in northern Itasca County. The sills were intruded into a sequence of mafic to felsic volcanic and volcanoclastic rocks that are part of a typical Archean greenstone belt, and have been deformed together with the enclosing volcanics. Following discovery of these rocks in the mid-1960's they were explored as a potential source of copper and nickel, but no concentrations of economic size and grade were discovered.

The report consists of two parts, written by different authors who worked in the area at different times and with different objectives in mind. It is only reasonable that their conclusions differ somewhat in detail, in view of the poor bedrock exposure in the area; indeed, it is surprising that they differ as little as they do. Thus, although the geologic maps that accompany each part of the report are not the same in detail, the basic framework of the geology is consistent throughout.

Part A, by John Berkley and Glen Himmelberg, formally defines the Deer Lake Complex and provides details on the silicate mineralogy of the sills that comprise it. Berkley and Himmelberg also discuss the fractional crystallization of the sills and develop a model for their crystallization.

Part B, by Edward Ripley, focuses on the petrology of the sulfide minerals in the sills. Ripley attributes the absence of significant Ni-sulfide accumulation to the relatively high FeO content of the parent magma and to iron enrichment during differentiation. The relatively high iron content of the melt throughout the crystallization process kept sulfur soluble in the magma, and prevented more than minor segregation of immiscible sulfide liquid at any stage.

The work reported here was supported by the Minnesota Geological Survey through grants to John L. Berkley while he was a student at the University of Missouri, Columbia, Missouri, and to Edward M. Ripley while he was a student at the University of Minnesota, Duluth.

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**CUMULUS MINERALOGY
AND PETROLOGY
OF THE DEER LAKE COMPLEX,
ITASCA COUNTY,
MINNESOTA**

By John L. Berkley and Glen R. Himmelberg

**GEOLOGY OF THE DEER LAKE COMPLEX,
ITASCA COUNTY, MINNESOTA**

MINNESOTA GEOLOGICAL SURVEY
Report of Investigations 20-A

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CUMULUS MINERALOGY AND PETROLOGY OF
THE DEER LAKE COMPLEX, ITASCA COUNTY, MINNESOTA

by

JOHN L. BERKLEY AND GLEN R. HIMMELBERG

ABSTRACT

The Deer Lake Complex, Itasca County, Minnesota is a series of gravity differentiated mafic sills intruded into tuffaceous metasedimentary rocks and pillowed metabasalts of Early Precambrian (Archean) age. Fragments or whole sections of three sills are represented in outcrop, each intruded along the upper contact of the previously intruded and solidified sill. Crystal fractionation produced a sequence of rock types, which from bottom to top are chilled hornblende basalt-gabbro, hornblende-augite peridotite, clinopyroxenite, augite gabbro, and hornblende diorite. Cumulus phases are chromite, olivine (Fe_{84}), augite ($En_{52}Wo_{38}Fs_{10}$), and plagioclase (An_{36} and An_{58}).

INTRODUCTION

The name Deer Lake Complex is proposed here for a series of super-imposed, stratiform, mafic-ultramafic sills that crop out over an extensive swamp and forest area in part of George Washington State Forest, about 4.8 km southwest of Deer Lake and about 6.5 km northeast of the town of Bigfork, northeastern Itasca County, Minnesota. Bedrock exposure is concentrated in a narrow, northeast-trending band, 10 km long and 2.5 km wide in portions of Tps. 62 and 61 N., and Rs. 25 and 24 W. (fig. 1), and this

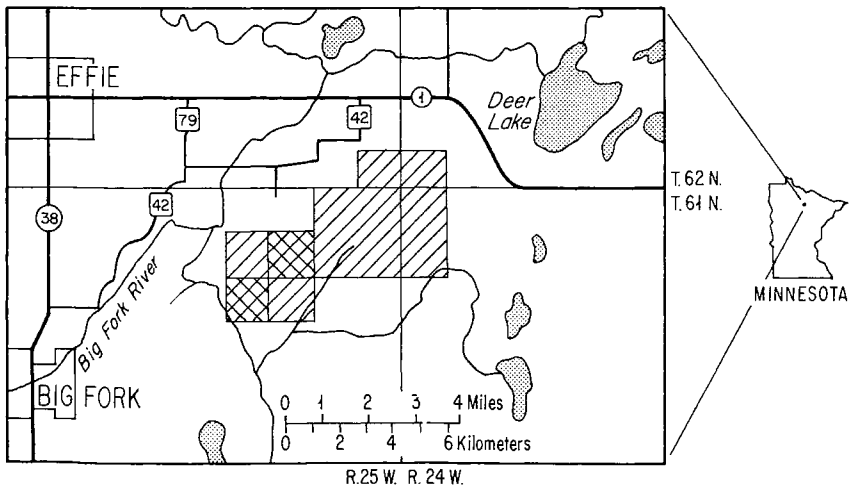


Figure 1 — Location map. Area of Figure 2, part B of this report is shown doubly cross hatched.

EXPLANATION

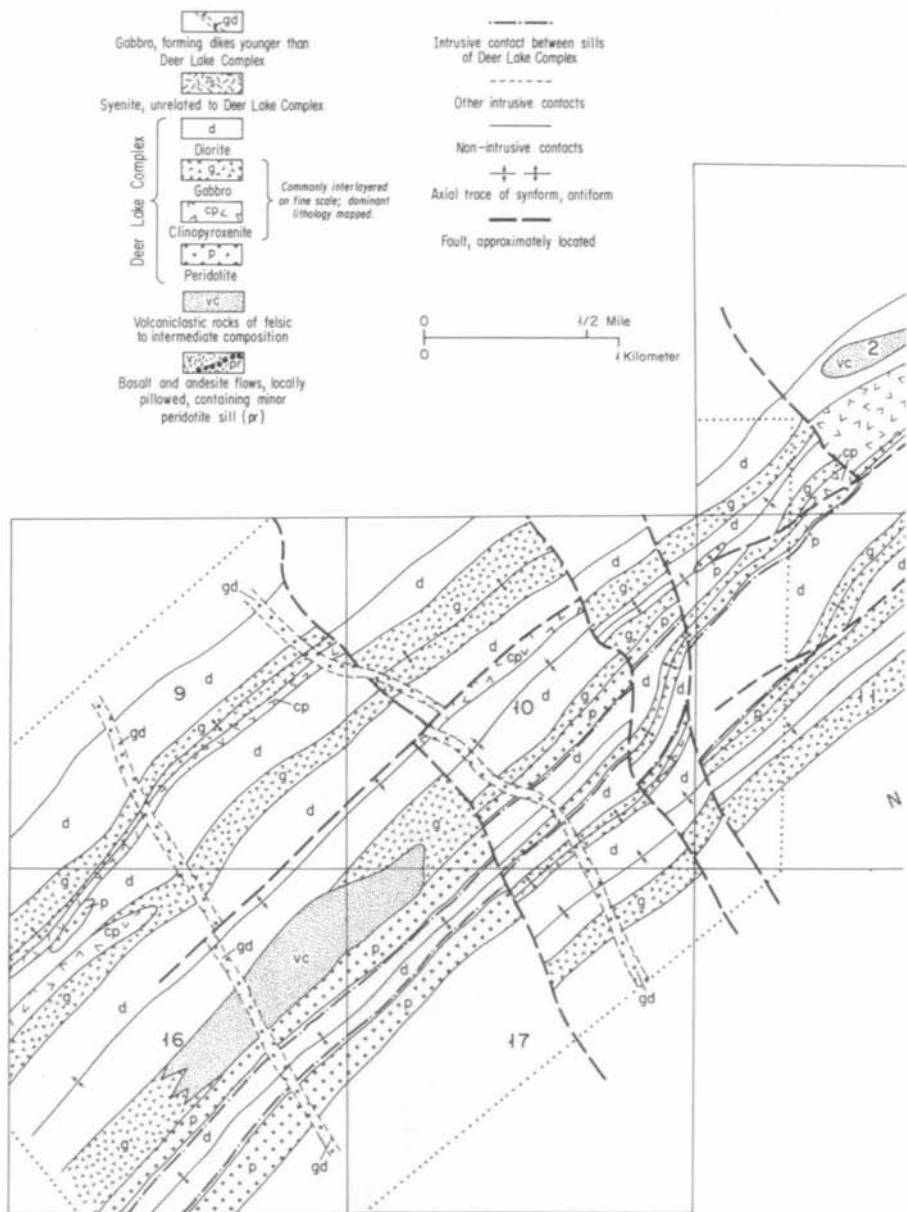


Figure 2 — Geologic map of the Deer Lake Complex. Generalized from field mapping at scale 1:9,600 (Berkley, 1972). Geology inferred where under glacial cover. The area studied by Ripley (1978, Figure 2, part B of this report, p. B3) is outlined by heavy dotted lines.

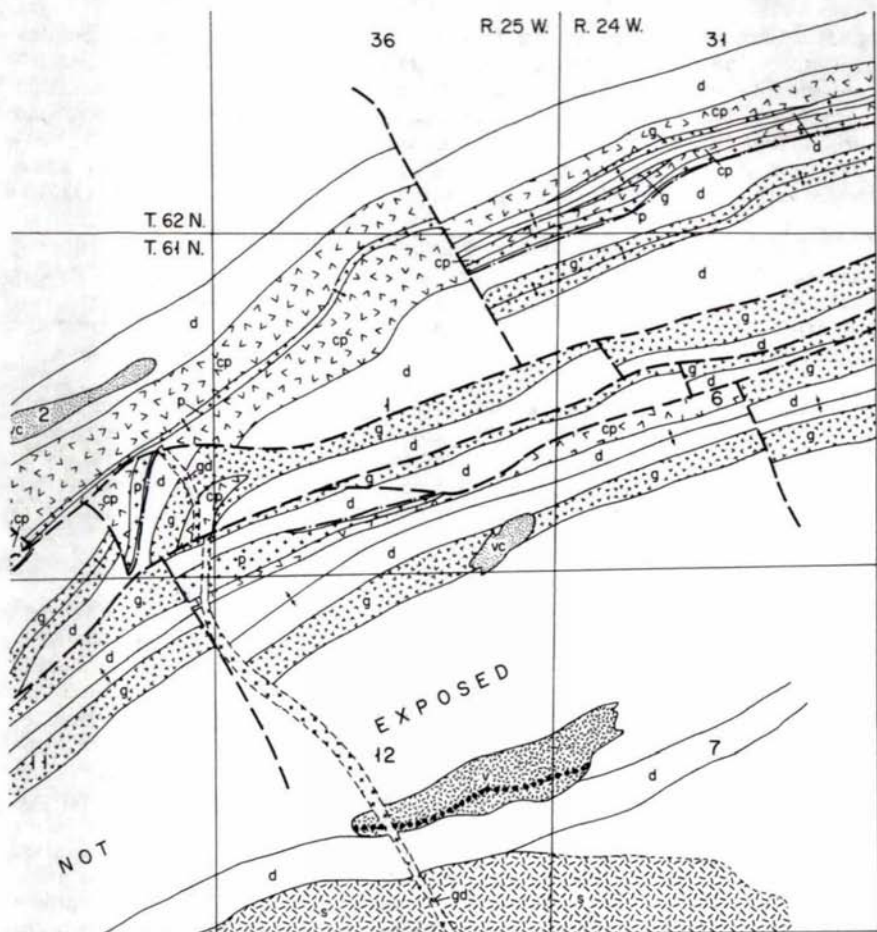


Figure 2 — continued

band is here designated as the type locality. The rocks of the complex consist of peridotite, pyroxenite, diorite and gabbro. The sills are conformable with an interbedded assemblage of pillowed and massive metabasalt and andesite, quartzofeldspathic metasedimentary rocks, and carbonaceous slates that compose a Lower Precambrian (Archean) "greenstone belt," possibly contemporaneous with the Ely or Newton Lake formations of the Vermilion district in northeastern Minnesota (Sims, 1972).

The Deer Lake Complex was shown but not named on the Hibbing Sheet of the Geologic Atlas of Minnesota (Sims and others, 1970). It was explored geologically by R.W. Ojakangas in 1966, and was of interest as a potential source of massive copper-nickel deposits from 1969 until recently (Ripley, 1973).

The Deer Lake Complex and its associated country rocks are folded about axes which trend N. 40°-50° E. and are broken by several faults. Northwest-trending, post-tectonic gabbroic dikes (fig. 2) that range in thickness from 15 to 30 m intrude the complex and are themselves faulted. Similar dikes have been dated by Hanson and Malhotra (1971) at 2.0 to 2.2 billion years.

At least two separate sills crop out at Deer Lake, and depending upon structural interpretation, a third sill is partially exposed. Only the upper units of the lowermost sill, consisting of augite gabbro and hornblende diorite, are exposed, whereas the middle and upper sills are completely exposed and consist from bottom to top of chilled basalt-gabbro, hornblende-augite peridotite, clinopyroxenite, augite gabbro, and hornblende diorite or quartz diorite. The middle and upper sills each are approximately 215 m thick. All three sills are in direct contact with each other without intervening country rock, although silicified metasedimentary inclusions are present locally, most commonly in the chilled basaltic margins. Chilled basalt grading into hornblende gabbro occurs at the base of the middle and upper sills. Figure 3 depicts an ideal stratigraphic section for the middle sill, portions of which are applicable to the exposed portions of the other two sills.

The Deer Lake sills are apparently quite similar to the sills of the Abitibi orogenic belt of the Superior Province of Canada (Goodwin and Ridler, 1970), especially the Munro Lake, Garrison, and Ghost Range sills (MacRae, 1969) and the Dundonald sill (Naldrett and Mason, 1968). Green (1972) has described similar differentiated sills in the Ely, Minnesota area. All of these sills, including Deer Lake, belong to what Naldrett (1972) designated as "small" gravity stratified sills ("1 to 10 miles long, up to 5,000 feet thick"); all possess stratified rock layers that are parallel to the stratification of the surrounding rocks, and all display evidence of emplacement prior to folding.

This paper reports the general petrologic aspects of the layered sill complex at Deer Lake, and includes electron microprobe analyses of cumulus phases. As a preliminary study, it does not include whole rock chemical analyses; it is hoped that it will stimulate further research leading to detailed delineation of chemical trends within the Deer Lake Complex.

Mode of Origin	Map Unit	Lithologies	Cumulus Minerals	Postcumulus Minerals
residual differentiates	diorite (D)	quartz-bearing hornblende diorite hornblende diorite	non-cumulate quartz, plagioclase, and hornblende	
cumulates	gabbro (G)	augite gabbro	plagioclase	augite (minor quartz)
	pyroxenite (CP)	clinopyroxenite	augite plagioclase	
			augite (minor orthopyroxene)	plagioclase augite
peridotite (P)	hornblende-augite peridotite	olivine chromite	hornblende augite	
chilled border		chilled hornblende gabbro	non-cumulate hornblende and plagioclase with minor cumulus chromite	

Figure 3 — Schematic stratigraphic column for middle sill, Deer Lake Complex. Chart is applicable to all sills. Symbols in parentheses under map units were used on Figure 2.

PETROGRAPHY

Chilled Border Rocks

At the base of the middle and upper sills is a fine-grained basaltic material which gradually becomes coarser upward from the intrusive contact and grades into a hornblende gabbro. These rocks are believed to represent the essentially unfractionated, primary basaltic magma chilled against an earlier cold, solidified sill. The fine-grained chilled rocks are light greenish gray on both weathered and fresh surfaces. Locally these rocks contain abundant limonite derived from oxidation of iron sulfide minerals that coat fractures. The coarser, gabbroic component of the chilled rocks is generally tan to brown or black where weathered, and black to dark green or gray on fresh surfaces.

Primary phases in the fine-grained material are invariably altered to actinolite and chlorite. The coarser grained rocks contain relict primary plagioclase laths poikilitically enclosed in brown hornblende. Some plagioclase laths display skeletal habits with rectangular interiors filled by amphibole (fig. 4). This is a further indication of chilled margin origin for these rocks because the presence of skeletal plagioclase can probably be ascribed to crystallization under supercooled conditions (Lofgren, 1974). Plagioclase is characteristically subordinate to hornblende in amount, and ranges from 20 to 30 percent in samples where alteration has not obliterated primary minerals. Alteration of plagioclase to epidote group minerals and hydrogrossular is common, and hornblende is commonly altered to actinolite.

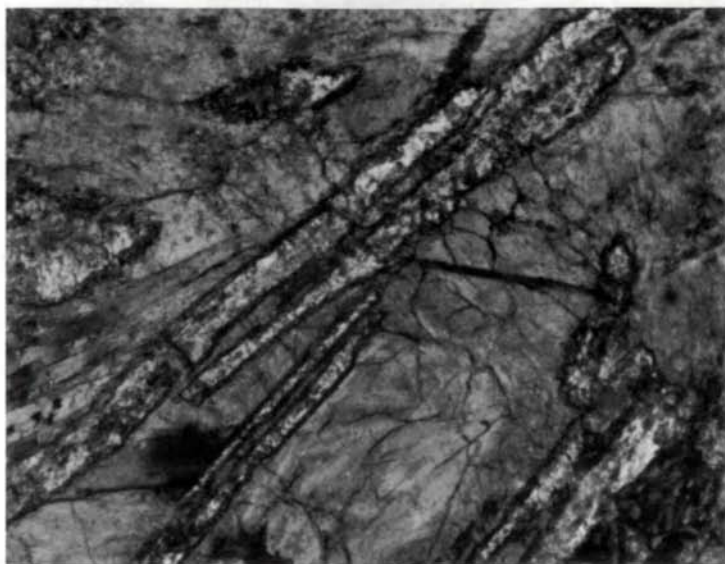


Figure 4 — Photomicrograph of skeletal altered plagioclase in chilled gabbro. Grains display hollow centers which may be open at one end or completely enclosed. Centers are filled by green amphibole, the major groundmass phase. Width of photograph = 3 mm.

Chromite grains with an average size of 0.3 mm occur in very minor amounts in the uppermost portions of the chilled gabbro units, but are absent from finer grained rocks nearer the intrusive contact. The absence of chromite from all but the upper parts of the chilled rocks, together with the presence of skeletal plagioclase that suggests crystallization in place (not cumulus), indicates that the mafic parent magma of the two upper Deer Lake sills was not precipitating mineral phases prior to intrusion. Chromite crystallization did not begin until shortly after the sills had been emplaced.

The chilled zones average from 5 to 10 m in thickness; the thickness varies slightly along strike.

Hornblende-augite Peridotite

Stratigraphically above and in sharp contact with the lower chilled zones of the two upper sills are layers of serpentinized hornblende-augite peridotite. Weathered outcrop surfaces of the peridotite are dark brown or various shades of gray; fresh surfaces are dark green to black. The peridotite generally possesses relatively strong magnetic properties because of its high content of secondary magnetite.

The peridotite layers contain two primary cumulus phases--chromite and olivine--and are the lowest units of the cumulate series (fig. 3). Much of the olivine, which originally composed from 60 to 80 percent of these rocks, has been serpentinized, and some has been altered to talc or talc-tremolite intergrowths. Original olivine grains range in size from less than 1 mm to as

large as 4 mm, and average about 1 mm. They range in shape from subhedral to euhedral and from equidimensional to elongate. Some olivine grains are rimmed by clinopyroxene, and some clinopyroxene rimmed olivine grains are altered to tremolite. Grain contacts between olivine and pyroxene (or amphibole) are serrated, suggesting a reaction relationship.

Chromite forms anhedral to euhedral grains smaller than 0.5 mm that are disseminated throughout the rock. Some chromite grains are enclosed in olivine. Some of the chromite is completely or partially altered to ferritchromite. (See Beeson and Jackson, 1969.)

Clinopyroxene and primary reddish-brown hornblende occur as post-cumulus minerals, typically as oikocrysts (fig. 5). They may coexist in the same rock sample or may occur individually. Hornblende oikocrysts are usually highly altered to actinolite plus chlorite. Carbonate minerals are also common alteration products of hornblende, as well as clinopyroxene. Most of the clinopyroxene is altered to tremolite. Some relict clinopyroxene grains possess thin, parallel exsolution lamellae of an unidentified phase.

Clinopyroxenite

In the middle and upper sills the peridotite layer is separated from the overlying clinopyroxenite layer by a sharp contact where cumulus olivine and chromite disappear and cumulus augite appears in quantity. The clinopyroxenite is light to medium green on both weathered and fresh surfaces and is composed almost exclusively of cumulus clinopyroxene.

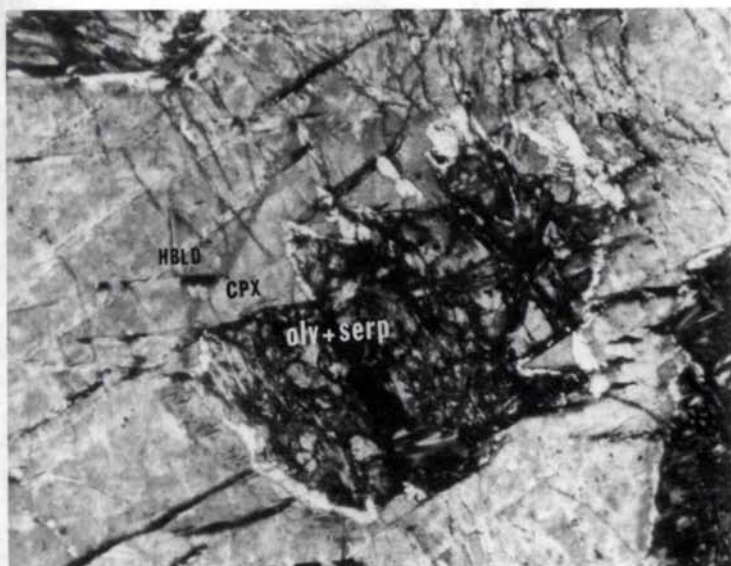


Figure 5 — Photomicrograph of olivine grain in peridotite with clinopyroxene reaction rim enclosed in a hornblende oikocryst. Width of photograph = 2.5 mm.

Augite composes from 80 to 95 percent of the rock and is the sole cumulus phase in most clinopyroxenite samples studied. Minor remnant cumulus orthopyroxene was identified tentatively in one thin section. Possible cumulus orthopyroxene grains are octagonal in habit where euhedral, and are pseudomorphed by serpentine plus tremolite. The cumulus clinopyroxene grains are subhedral to euhedral with elongated octagonal habits, are typically smaller than 1 mm long, and are generally altered to tremolite.

Postcumulus minerals in the clinopyroxenite are interstitial plagioclase, yielding an orthocumulate (Wager and others, 1960), and adcumulate augite (fig. 6). Adcumulates are more prevalent toward the bottom of clinopyroxenite units, where plagioclase is rare or absent. This may mean that pyroxene production and accumulation proceeded more rapidly in the early stages of pyroxene crystallization than in the later stages (Hess, 1960).

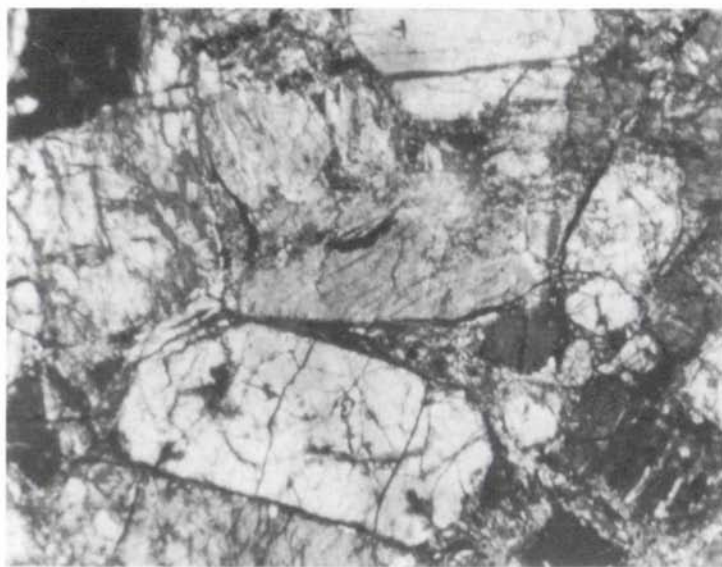


Figure 6 — Photomicrograph of adcumulate texture in clinopyroxenite. Note euhedral augite grains in an augite matrix. Such textures are more prevalent near basal portions of clinopyroxenite units; plagioclase becomes the intercumulus phase at higher stratigraphic positions.

Augite Gabbro

The contact between the clinopyroxenite and the overlying augite gabbro is marked by the appearance of cumulus plagioclase in addition to cumulus clinopyroxene. At a somewhat higher stratigraphic horizon plagioclase becomes the sole cumulus phase. The augite gabbro is light green to gray in outcrop and gray on fresh surfaces. Because its color and textural characteristics in outcrop are similar to those of the feldspathic clinopyroxenites described below, they are difficult to distinguish in the field.

Cumulus augite, where present, is similar to that in the clinopyroxenite. Cumulus plagioclase in the augite gabbro generally occurs as euhedral laths, rarely longer than 1 mm, and composes from 30 to 50 percent of the rock. It is commonly altered to epidote group minerals and granular, isotropic phases, possibly including hydrogrossular.

The chief postcumulus phase in the augite gabbro is augite that typically is more or less altered to actinolite or actinolite plus chlorite. Postcumulus quartz occurs locally in amounts no greater than 1 or 2 percent. Minor amounts of interstitial sulfide minerals are also present.

Hornblende Diorite

A layer of hornblende diorite and quartz-bearing or granophyric hornblende diorite occurs above the augite gabbro in all sills of the Deer Lake Complex. The contact between the augite gabbro and hornblende diorite is gradational over a thickness of a few meters and is marked by an upward increase in grain size and a change from clinopyroxene to primary green hornblende as the principal mafic phase. No evidence for an intrusive contact between gabbro and diorite units was found. Anorthite content of plagioclase as determined by qualitative electron microprobe analysis decreases across the contact with no apparent break in composition. The diorite, therefore, is considered to represent the volatile and silica-enriched residua remaining after differentiation by gravity settling had been completed.

The hornblende diorite is light to dark gray on weathered surfaces, and commonly displays a texture of plagioclase and intergranular, semi-radiating black hornblende blades, some of which attain lengths of 4 to 5 cm. Fresh surfaces are black to dark green in color.

The principal phases in the hornblende diorite are plagioclase and green hornblende. Plagioclase is generally somewhat altered to epidote group minerals, but is remarkably fresh in some samples. It is commonly euhedral and possesses both carlsbad and albite twinning.

Green hornblende is generally anhedral and partially surrounds the plagioclase laths. Some is twinned along the crystallographic axis and most is altered to actinolite plus chlorite. Hornblende is considered a primary igneous phase in the diorite, although it could represent a deuteric or metamorphic alteration of pyroxene. It may be noted, however, that clinopyroxene occurring in the augite gabbro beneath the diorite is rarely altered completely to amphibole; moreover, the absence of amphibole with clinopyroxene cores in the diorite would indicate a secondary origin for the amphibole.

Quartz occurs in the hornblende diorite either as distinct anhedral grains or intergrown with sodic plagioclase as micrographic or granophyric intergrowths. Quartz-rich diorite tends to appear at higher stratigraphic positions than quartz-poor diorite, but exceptions occur.

Micropegmatite veins that range in thickness from less than 3 cm to 10 cm are locally abundant in the hornblende diorite. They contain semi-

radiating or randomly oriented hornblende blades and plagioclase laths which range from 5 to 10 cm in length. Well developed micrographic intergrowth of quartz and alkali feldspar is invariably present. Micropegmatite veins were observed in all rock types in the Deer Lake Complex except the peridotite. In the clinopyroxenite they contain enlarged augite and plagioclase grains without the quartz-feldspar intergrowths found in the more feldspathic units above.

The diorite layers of the lower and middle sills are capped by an "amphibolitic fraction" composed of 70 to 95 percent actinolite and/or hornblende with plagioclase, carbonate minerals, epidote group minerals, and locally with minor quartz. The rock is characterized by long, semiradiating amphibole crystals which may attain lengths of 7 cm or more (fig. 7). This rock may have formed by contact metamorphism of the uppermost hornblende diorite and upper chilled zone, and will be discussed in more detail below.



Figure 7 — Hand specimen of amphibolitic fraction of the upper margins of sills. Note long semi-radiating amphiboles.

CUMULUS MINERAL CHEMISTRY

Representative chemical analyses of cumulus minerals from the peridotite, clinopyroxenite and augite gabbro units of the Deer Lake Complex are given in Table 1. The analyses were done on an Applied Research Laboratories EMX-SM electron microprobe at the University of Missouri, Columbia. Quantitative analyses were done using 15 KV accelerating potential and 350 microamperes emission current, and were corrected for background, absorption, fluorescence and atomic number. Plagioclase was analyzed using 0.02 microampere specimen current; all other minerals were run at 0.03 microamperes. All standards except plagioclase were mineral phases from the alpine peridotite at Burro Mountain, California. The plagioclase standard was synthetic.

Chromite and Ferritchromite

Chromite occurs mainly in the peridotite and less abundantly in the chilled basalt. Microprobe analyses of selected chromite grains in peridotite indicate that most of the primary chromite has been altered partly or wholly to ferritchromite. Only one sample was found to contain primary chromite in sufficient quantity for analysis. This chromite composition (tbl. 1, column 1) contrasts with the associated ferritchromite (tbl. 1, column 2) by being richer in Cr_2O_3 and poorer in FeO and TiO_2 . These results correspond well with compositions of ferritchromite and parent chromite from the Stillwater Complex, Montana, determined by Beeson and Jackson (1969).

The fresh chromite analyzed was slightly zoned with Cr_2O_3 , Al_2O_3 and MgO increasing inward, and FeO and TiO_2 decreasing correspondingly.

Olivine

Olivine, generally much altered to serpentine, occurs exclusively in the peridotite. One well exposed section of peridotite from the middle sill was sampled at 6-m intervals to determine what variation there is in olivine composition with increasing distance above the base. Relatively fresh olivine was found in only three specimens, taken at 21, 27 and 64 m above the base of the unit. The analyses of olivine from these rocks are given in Table 1 (columns 3, 4, and 5); they are remarkably similar, averaging Fo_{84} . MacRae (1969) reported a range of Fo_{64} - Fo_{78} over a 150-m section in the Centre Hill section of the Munro Lake sill, Canada, but found little variation in composition within sections equivalent in thickness to those sampled at Deer Lake (43 m). In a review of olivine-rich rocks from small intrusions, Drever and Johnston (1967) reported olivine compositions restricted within the range Fo_{77} - Fo_{85} . Other intrusions with olivine compositions similar to those of the Deer Lake Complex are the Shiant Isles picrite (Walker, 1930) with Fo_{84} , and the Uwekahuna laccolith, Hawaii (Murata and Richter, 1961) with Fo_{85} .

Clinopyroxene

Cumulus clinopyroxene was analyzed from the clinopyroxenite directly above the peridotite from which olivine was analyzed. The analyses of three samples are given in Table 1 (columns 6, 7, and 8). Little significant chemical variation was found in these pyroxenes, and none was expected since the lowest and highest specimens were taken only 6 m apart. Alteration of pyroxene is widespread and residual fresh pyroxene is scarce. The average composition of clinopyroxene is $\text{En}_{52}\text{Wo}_{38}\text{Fs}_{10}$, which plots in the augite field of the standard pyroxene quadrilateral. It is sufficiently chrome-rich to be termed a chromian augite (Deer and others, 1966).

Plagioclase

Plagioclase is the major cumulus phase in the augite gabbro, and was sampled in a manner identical to that described for olivine and clinopyroxene. Only one sample from the middle sill was acceptable for analysis and is

Table 1 — Electron microprobe analyses of cumulus minerals
(---, not determined).

	PERIDOTITE				
	(1) Chromite	(2) Ferrit- chromite	(3) Olivine	(4) Olivine	(5) Olivine
SiO ₂	0.27	0.20	40.7	39.8	40.4
TiO ₂	0.21	1.16	0.03	0.03	0.04
Al ₂ O ₃	18.9	13.3	---	---	---
Cr ₂ O ₃	43.4	33.3	0.01	0.03	0.01
Fe ₂ O ₃	6.7	19.0	---	---	---
FeO	18.4	31.0	14.9	16.2	13.7
MnO	0.79	0.30	0.20	0.24	0.20
MgO	10.1	2.47	44.5	42.6	45.0
CaO	0.17	0.24	0.23	0.25	0.22
Na ₂ O	---	---	---	---	---
K ₂ O	---	---	---	---	---
Total	98.94	100.97	100.80	99.40	99.88

Cations on basis of 32 oxygen atoms for spinels and 4 for olivine

Si	0.069	0.055	1.012	1.012	1.009
Al	5.721	4.298	---	---	---
Ti	0.041	0.239	0.001	0.001	0.001
Cr	8.813	7.219	0.000	0.001	0.000
Fe ³⁺	1.295	3.920	---	---	---
Fe ²⁺	3.952	7.107	0.310	0.344	0.286
Mn	0.172	0.070	0.004	0.005	0.004
Mg	0.866	1.009	1.649	1.614	1.675
Ca	0.047	0.070	0.006	0.007	0.006
Na	---	---	---	---	---
K	---	---	---	---	---
A	15.939	15.731	---	---	---
B	8.037	8.256	---	---	---
Z	---	---	1.012	1.012	1.009
XY	---	---	1.974	1.979	1.978
SUM	23.976	23.987	2.986	3.001	2.987

End-Members

Sp	35.9	12.69	---	---	---
Herc	0.0	14.32	---	---	---
Ulv	1.2	3.0	---	---	---
Pi	12.64	0.0	---	---	---
Chr	42.7	45.37	---	---	---
Fo	---	---	84.2	82.4	85.4
Fa	---	---	15.8	17.6	14.6
En	---	---	---	---	---
Wo	---	---	---	---	---
Fs	---	---	---	---	---
An	---	---	---	---	---
Or	---	---	---	---	---
Ab	---	---	---	---	---

Table 1 — continued.

CLINOPYROXENITE			GABBRO		
(6)	(7)	(8)	(9)	(10)	
Clino- pyroxene	Clino- pyroxene	Clino- pyroxene	Plagio- clase	Plagio- clase	
52.3	52.3	52.3	56.6	53.0	SiO ₂
0.15	0.14	0.13	---	---	TiO ₂
1.72	1.91	2.02	28.3	29.7	Al ₂ O ₃
2.08	1.50	1.53	---	---	Cr ₂ O ₃
---	---	---	---	---	Fe ₂ O ₃
6.8	6.6	6.6	0.59	0.83	FeO
0.19	0.21	0.21	---	---	MnO
19.1	18.7	18.8	---	---	MgO
17.9	18.6	18.5	5.3	12.4	CaO
0.18	0.20	0.21	6.0	4.9	Na ₂ O
---	---	---	1.74	0.11	K ₂ O
100.42	100.16	100.30	100.27	101.05	Total

Cations on basis of 6 oxygen atoms for clinopyroxene and 32 for plagioclase

1.913 } Z	1.917 } Z	1.914 } Z	10.148 } Z	9.565 } Z	Si
0.074 } Z	0.083 } Z	0.087 } Z	5.981 } Z	6.318 } Z	Al
0.004 } Z	0.004 } Z	0.004 } Z	---	---	Ti
0.060 } Z	0.043 } Z	0.044 } Z	---	---	Cr
---	---	---	---	---	Fe ³⁺
0.208 } XY	0.202 } XY	0.202 } XY	0.088 } XY	0.125 } XY	Fe ²⁺
0.006 } XY	0.007 } XY	0.007 } XY	---	---	Mn
1.041 } XY	1.022 } XY	1.026 } XY	---	---	Mg
0.702 } XY	0.731 } XY	0.726 } XY	1.402 } XY	2.398 } XY	Ca
0.013 } XY	0.014 } XY	0.015 } XY	2.086 } XY	1.715 } XY	Na
---	---	---	0.396 } XY	0.025 } XY	K
---	---	---	---	---	A
---	---	---	---	---	B
1.987	2.000	2.001	16.129	15.883	Z
2.034	2.023	2.024	3.972	4.263	XY
4.021	4.023	4.025	20.101	20.146	SUM

End-Members

---	---	---	---	---	Sp
---	---	---	---	---	Herc
---	---	---	---	---	Ulv
---	---	---	---	---	Pi
---	---	---	---	---	Chr
---	---	---	---	---	Fo
---	---	---	---	---	Fa
25.4	39.8	32.2	---	---	En
73.7	59.7	67.2	---	---	Wo
0.93	0.46	0.66	---	---	Fs
---	---	---	36.1	57.9	An
---	---	---	10.2	0.61	Or
---	---	---	53.7	41.4	Ab

presented in Table 1 (column 9). The composition of plagioclase from the augite gabbro of the lower sill is given for comparison in column 10 of Table 1. The composition of plagioclase from the middle sill is more alkaline than that in the lower sill and contains 10 percent normative Or. The lower sill plagioclase composition is An_{58}, Or_{61} .

A qualitative analysis using the electron microprobe was performed on altered plagioclase grains from different stratigraphic levels within the augite gabbro and hornblende diorite layers. Anorthite content decreases progressively with increasing stratigraphic height, and grades smoothly from the augite gabbro into the hornblende diorite.

DISCUSSION

The sequence of rock types encountered in the Deer Lake Complex can be explained as a series of three conformable, horizontally emplaced mafic magma intrusions. Each magma injection fractionated into ultramafic through dioritic rock types and was wholly or mainly solidified before the next intrusion of new magma. Each new injection of magma utilized the upper surface of the previous sill as a structural control, and the process of gravity fractionation was then repeated in the new sill. Thus, the complex grew stratigraphically upward through time, shouldering apart some country rock, but mainly incorporating it as large inclusions, some of which possibly exceed 150 m in thickness. Examination of chilled zones provides the following evidence for the upward growth of the complex:

- (1) Chilled rocks are known only from the basal portions of the sills. They are composed of basalt that becomes coarser upward, toward the overlying peridotite unit (fig. 3).
- (2) Chilled basalt is invariably in direct contact with the "amphibolitic fraction" that forms the top of the next lower sill. There are no discernible chilled rocks exhibiting progressive grain coarsening downward toward the amphibolitic fraction. Therefore it appears that the amphibolitic fractions are upper chilled basalts that were recrystallized beyond recognition by the superheat of the overlying mafic magma, which was above its liquidus temperature (or at least not forming phenocrysts) when it was intruded. Thus, the upper chilled margins and locally the uppermost part of the hornblende diorite were metamorphosed to become the amphibolitic fraction.
- (3) The mineralogy and rock fabric displayed by the amphibolitic fraction resemble those of amphibolite and mafic hornfels that have formed in thermal aureoles. (See Shido, 1958; Compton, 1958.) Although the possibility exists that the amphibolitic fraction represents a mafic pegmatite (John C. Green, 1972, oral commun.), this does not account for the missing upper chilled rocks, which presumably formed during intrusion of the sills.

Subsequent to intrusion, the basaltic magmas composing the sills began to fractionate. The sequence of precipitated cumulus phases is illustrated in Figure 8. Chromite was the initial phase to crystallize, followed shortly thereafter by olivine. Settling of olivine and chromite resulted in the formation of peridotite. Sometime later, the coprecipitation of olivine and

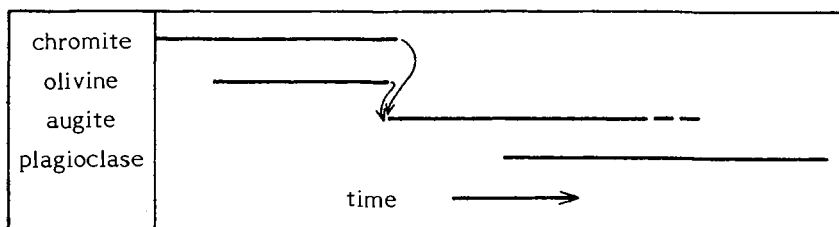


Figure 8 — Diagram of crystallization sequence of cumulus phases. Arrows indicate probable reaction relationships.

chromite ceased, and was followed immediately by crystallization of augite, producing the clinopyroxenite. The reaction of olivine with liquid to produce clinopyroxene can be followed on the liquidus diagram for the system diopside-forsterite-silica (fig. 9; Kushiro and Shairer, 1963; Kushiro, 1972). The composition of the primary mafic melt must lie within the shaded field in Figure 9 in order for the liquid path to intersect the boundary curve on the right side of the thermal divide separating olivine-diopside cotectic and reaction relations. Precipitation of orthopyroxene would occur in compositions below the shaded area, an occurrence of limited importance if it occurred at all. The composition of any liquid lying within the shaded area in Figure 9 is tholeiitic, as is also indicated by the presence of clinopyroxene reaction rims on peridotite olivine grains.

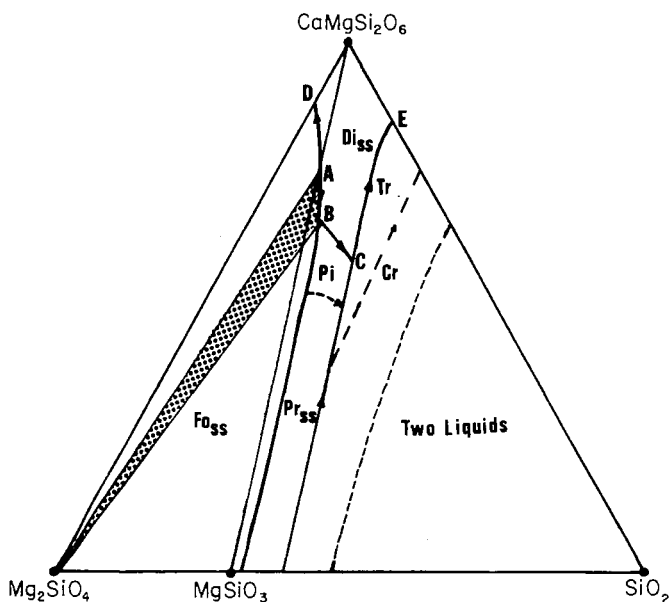


Figure 9 — Liquidus diagram at 1 atmosphere for the system diopside-forsterite-silica (Kushiro and Schairer, 1963; Kushiro, 1972). Shaded area denotes limits of composition field of Deer Lake primary magma. Fo_{SS} = forsterite solid solution; Di_{SS} = diopside solid solution; Pi = pigeonite; Pr_{SS} = protoenstatite solid solution; Tr = tridymite; Cr = cristabolite.

The reaction of chromite to produce clinopyroxene has been discussed by Irvine (1967). The abrupt termination of chromite crystallization (none occurs in the clinopyroxenite units) indicates a peritectic relationship of chromite to augite. The clinopyroxene was able to accommodate all of the Cr_2O_3 remaining in the magma at this stage, thereby suppressing the crystallization of a chromian spinel.

The removal of olivine by crystal settling probably caused the liquid path to trend directly across the diopside field (fig. 9), resulting in early crystallization of large volumes of clinopyroxene crystals. Eventually the liquid path intersected a pyroxene-plagioclase cotectic, causing precipitation and settling of both augite and plagioclase to produce the augite gabbro. The lagging behind of plagioclase relative to augite during settling, or perhaps plagioclase floatation, may have resulted in the fact that the upper augite gabbro contains only plagioclase as a cumulus phase, although it is also possible that plagioclase production continued longer than augite crystallization, as shown in Figure 8.

CONCLUSIONS

The Deer Lake Complex consists of three separate mafic intrusions, each of which fractionated to produce very similar rock sequences. MacRae (1969) explained the cyclic alternation of rocks in the Munro Lake sill, Canada, by magma refreshment, which is quite reasonable considering the non-intrusive gradational nature of the contact between cyclic units at Munro Lake. However, the two sills completely exposed at Deer Lake must be considered single magma injections (not cyclic units) because their contacts with intrusive rocks above and below are marked by chilled basaltic margins. The basal part of the lowermost sill is not exposed and its character below the augite gabbro is unknown. Its gabbro and diorite units, however, are petrographically so similar to the corresponding units of the middle and upper sills that a similar composition and structure can be inferred. This apparent similarity of successive magma types through time plus the absence of suspended crystals in the chilled rocks may imply direct derivation and rapid ascent from a mantle source, rather than from a fractionating magma chamber. Multiple injection of closely spaced basaltic magmas into an area no greater than 80 km^2 suggests that the area may have been a major center for volcanic activity, with eruptions being periodic and widely spaced through time.

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**SULFIDE MINERALS IN
THE LAYERED SILLS OF
THE DEER LAKE COMPLEX,
ITASCA COUNTY,
MINNESOTA**

By Edward M. Ripley

**GEOLOGY OF THE DEER LAKE COMPLEX,
ITASCA COUNTY, MINNESOTA**

MINNESOTA GEOLOGICAL SURVEY
Report of Investigations 20-B

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SULFIDE MINERALS IN THE LAYERED SILLS OF THE
DEER LAKE COMPLEX, ITASCA COUNTY, MINNESOTA

by

EDWARD M. RIPLEY

ABSTRACT

The Deer Lake Complex is a sequence of mafic-ultramafic igneous rocks in an Archean greenstone belt of north-central Minnesota. The Complex consists of at least two ultramafic lenses, a gabbroic body whose basal part is not exposed, and two layered sills that intrude a volcano-sedimentary sequence. The sills are differentiated into layers of peridotite, clinopyroxenite, two-pyroxene porphyritic gabbro, nonporphyritic gabbro, and sporadic quartz diorite cap rocks. Chilled-margin textures indicate supercooling. Metamorphism of the Complex and associated rocks is of the greenschist facies.

Minor amounts of sulfides and primary oxides are disseminated throughout the layered sills. Textural evidence and phase relations suggest that pyrrhotite, pentlandite, and chalcopyrite within basal chilled margins formed from an immiscible sulfide liquid which segregated prior to or soon after magma emplacement. The bulk composition of sulfide phases in basal chilled margins suggests that the sulfide assemblage represents a mixture of a Ni-bearing pyrrhotite solid solution and a Cu-rich liquid.

The primary sulfide minerals in the differentiated parts of the layered sills range from Ni-rich in peridotite units through Cu-rich in clinopyroxenite and lower porphyritic gabbro units to Fe- and S-rich in upper gabbro units. Sulfide minerals in peridotite, pyroxenite, and lower porphyritic gabbro units are thought to have formed from an immiscible sulfide liquid which segregated during silicate differentiation. Intergrowths of chalcopyrite, ilmenite, and magnetite in upper gabbro units probably formed directly from the silicate magma. Textural evidence in some upper gabbro and quartz diorite units suggests that pyrite has replaced Fe²⁺-bearing silicate minerals, probably in response to activity of a late sulfur-bearing residual fluid.

The absence of economic concentrations of Ni-sulfides associated with the sills is attributed to the relatively low MgO content of the parent magma and iron enrichment during differentiation. The relatively high FeO content of the melt rendered sulfur soluble in the magma, resulting in only minor amounts of sulfide liquid segregating prior to or during crystallization of the sills.

INTRODUCTION

The Deer Lake Complex is a 13-km-long by 3-km-wide belt of Lower Precambrian ultramafic and gabbroic rocks located 6.4 km southeast of the town of Effie, Itasca County, Minnesota (fig. 1). Magnetic anomalies associated with the Complex extend from the southern tip of Deer Lake to just northeast of the town of Bigfork. The Deer Lake Complex consists of at least two ultramafic lenses, a gabbroic body whose basal zone is not exposed, and two layered sills composed of peridotite, pyroxenite, and several kinds of gabbro (fig. 2). These rocks are intrusive into a volcano-sedimentary sequence containing metabasalt, metagraywacke, slate, and argillite. Precambrian felsic plutonic bodies flank the entire sequence to the northwest and southeast; for regional geology see the Hibbing Sheet of the Geologic Map of Minnesota (Sims and others, 1970). Drill core and outcrop data suggest that the sills of the Complex were emplaced either one beneath or one above the other within the sequence of basalts and metasediments. The intrusive rocks of the Complex have undergone initial isoclinal folding, followed by both normal and strike-slip faulting. The axes of antiforms and synforms produced during folding trend $\approx N 45^{\circ} E$. (See Ripley, 1973, for a discussion of the structural evolution of the Complex.) Metamorphism of the Complex and associated rocks is of the greenschist facies. Unmetamorphosed diabase dikes are found in many localities within the area. Similar dike swarms throughout northeastern Minnesota have yielded K-Ar ages of 2.0 to 2.2 billion years (Hanson and Malhotra, 1971), and it is believed that the diabase dikes in the Deer Lake area are part of this Middle Precambrian swarm (P.K. Sims, oral commun., 1973). The regional geologic setting is typical of cratonal granite-greenstone belt terranes as described by Anhaeusser and others (1969).

Airborne geophysical anomalies associated with the Complex were detected at about the same time that massive Ni-sulfide deposits associated with Archean ultramafic lenses were receiving widespread petrologic attention in both Canada and Western Australia (Naldrett, 1969; McCall and Leishman, 1971). Reconnaissance mapping by John Berkley for the United States Steel Corporation showed that the Complex was situated in Archean terrane similar to that which hosts the Canadian and Australian Ni deposits,

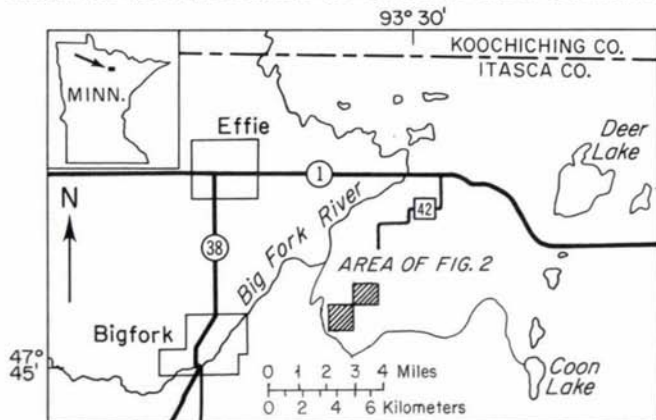


Figure 1 — Location map.

and that the Complex could be a potential source for Ni-sulfide ores. After extensive geophysical and geological studies, including diamond drilling, exploration in the area ceased. Although minor amounts of metallic sulfides occur in the sills of the Complex, no economic concentrations were located.

The purpose of this paper is to present the results of studies concerning the sulfide (+ oxide) petrology of the Deer Lake Complex, and to assess possible reasons why massive Ni-sulfide ores are not found associated with rocks of the Complex.

Techniques

Samples for petrographic and chemical analyses were collected from bedrock exposures and from more than 20 diamond drill cores made available by the United States Steel Corporation and the Hanna Mining Company. Petrographic modal analyses were based on point counting methods, with

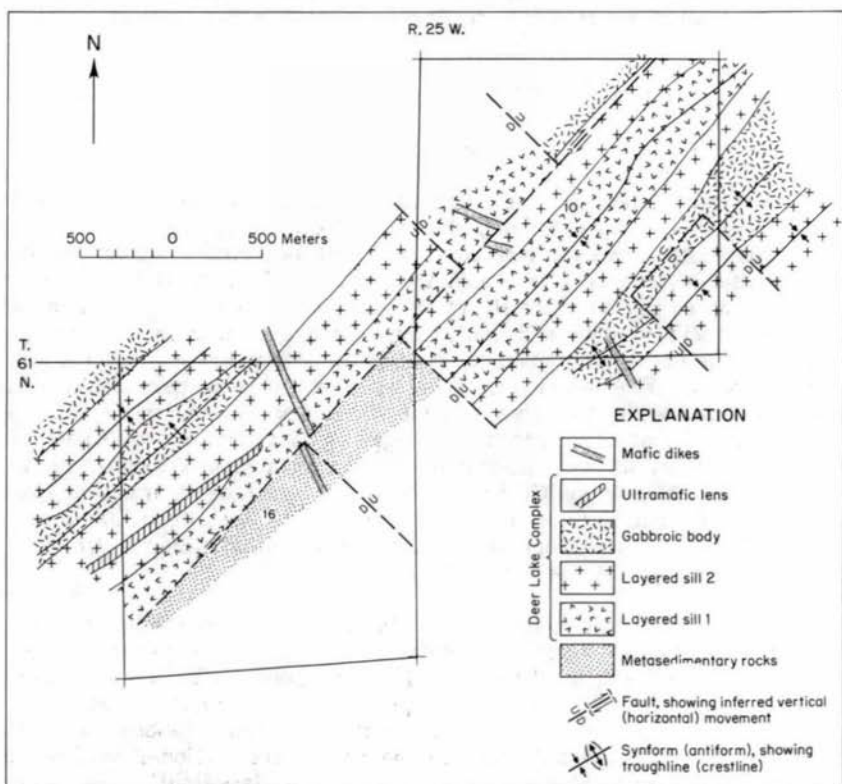


Figure 2 — Geologic map of part of the Deer Lake Complex. Generalized from field mapping (Ripley, 1973) augmented by diamond drilling. Note that the second ultramafic lens mentioned in the text occurs to the east of the illustrated map area. The location of this area relative to the larger area mapped by Berkley and Himmelberg (1978, part A of this volume) is shown on page A2.

1,000 points counted over a standard thin section for igneous rocks. Volume percentages of sulfide and oxide minerals examined in polished sections were determined by measuring the size of the grains within 100 fields of view. The observed sizes were summed and relative percentages calculated with respect to the total area of the fields. Electron microprobe analyses of major constituents of olivine, pyroxene, and sulfide minerals from the layered sills were made on an M.A.C. microprobe at the University of Minnesota, Minneapolis. The methods of microprobe analyses and data reduction were similar to those described by Grant and Weiblen (1968). Analyses are believed to be accurate to within ± 5 percent of the amount present for major constituents. Trace amounts of Cu and Ni were determined by atomic absorption techniques. Samples for such analyses were prepared by crushing in a steel-jaw crusher and grinding to -100 mesh in a disc pulverizer. Whole rock samples were dissolved in HCl, HNO₃, and HF. Analyses were performed using a Perkin-Elmer 303 Atomic Absorption Spectrophotometer located at the Department of Natural Resources, Division of Minerals, Hibbing, Minnesota. The detection limit of the analytical method is 1 ppm for Cu, 2 ppm for Co, and 3 ppm for Ni.

GEOLOGY OF THE DEER LAKE COMPLEX

General Features

The Deer Lake Complex has at its base a gabbroic intrusion of unknown thickness but presumed sheet-like form. Two layered sills occur stratigraphically above the intrusion. At least two ultramafic lenses occur between the layered sills, although they are locally discordant. Evidence from drill cores and outcrops shows that the layered sills range in thickness from 150 to 215 m. The ultramafic lenses average 40 m in their thickest portions. The base of the gabbroic body is not exposed in outcrop, nor has it been penetrated by drilling. However, at least 120 m of gabbroic material was recognized from drill core and the similarity between these rocks and the gabbro units of the layered sills suggests that the gabbro is part of a layered sequence, with ultramafic units existing at depth. The ultramafic lenses in the Deer Lake Complex are peridotite that is mineralogically similar to the basal peridotite of the layered sills. Basaltic chilled margins enclose the lenses and except for the absence of sulfide minerals are similar to chilled margins of the layered sills.

The layered sills consist of a basal chilled zone (3-6 m thick), physically overlain by layers of peridotite (30-60 m), clinopyroxenite (≈ 30 m), gabbro (90-125 m), local patches of quartz diorite (≈ 20 m), and a chilled upper marginal zone (6-12 m). The large lateral extent of the layers and the presence of cumulus textures in all but the uppermost gabbro and chilled zones suggest that the sills formed mainly by gravitational settling and accumulation of mineral grains. Table 1 gives a classification of the rock types present in Deer Lake layered sills.

The mineralogy and sequence of differentiation in the sills is similar to that reported in small Archean sills from greenstone belts in northeastern Minnesota (Schulz, 1974, 1977), Canada (Naldrett and Mason, 1968; MacRae, 1969; Arndt and others, 1977), Western Australia (Williams and Hallberg, 1973), and South Africa (Viljoen and Viljoen, 1970).

Table 1 — Classification of igneous rocks in the Deer Lake layered sills.

Classification Not Based on Cumulus Phases:

<u>Rock Type</u>	<u>Percent</u>	<u>Mineral Assemblages</u>
Quartz Diorite	45-50	Plagioclase
	20-25	Quartz
	10-30	Sulfides
	5-10	Amphibole
Upper Gabbros:		
Granophyric Gabbro	35	Clinopyroxene
	40-45	Plagioclase
	10-15	Granophyric Intergrowths
	5	Quartz
	8-10	Oxides+Sulfides
Quartz Gabbro	35-40	Clinopyroxene
	45	Plagioclase
	10	Quartz
	8-10	Oxides+Sulfides
Gabbro	35-40	Clinopyroxene
	50-55	Plagioclase
	8-10	Oxides+Sulfides

Classification Based on Cumulus Phases:

<u>Rock Type</u>	<u>Cumulus Phases</u>		<u>Intercumulus Phases</u>	
	<u>Percent</u>	<u>Mineral Assemblages</u>	<u>Percent</u>	<u>Mineral Assemblages</u>
Porphyritic Gabbro	20	Orthopyroxene	5-10	Plagioclase
	30	Clinopyroxene	3-5	Oxides+Sulf .
	40	Plagioclase		
Clinopyroxenite	70-80	Clinopyroxene	3-8	Plagioclase
	10-20	Orthopyroxene	0-2	Oxides+Sulf .
Peridotite	55-75	Olivine	25-30	Clinopyroxene & Hornblende
	2-3	Chromite		

Petrography of the Layered Sills

Because sulfide minerals are intimately associated with silicates in the Deer Lake Complex, it is essential to understand the variations in silicate mineralogy of the sills. Additional information regarding the igneous petrology of the sills is given in a report by John Berkley and Glen Himmelberg (1978).

Chilled Margins

The sills of the Deer Lake Complex have complex chilled margins. Because these margins are juxtaposed, and because shearing is common along contacts, the reconstruction of complete chilled margins is difficult. However, complete chilled zone sequences occur in at least two outcrop exposures and in several drill cores.

Lower chilled zones typically range from 3 to 6 m in thickness, whereas upper chilled zones range from 6 to 12 m. Both upper and lower chilled margins can be divided into three separate units, based primarily on crystal morphology. The outermost unit (A) is a fine-grained (0.1 mm) basaltic rock composed of nearly equal amounts of actinolite (after augite) and saussuritized plagioclase, with interstitial sulfide concentrations up to 4 percent. This unit is generally less than 2 m thick. The middle unit (B) is characterized by medium- to coarse-grained (0.15-2.5 cm) subradiating, skeletal prisms or needles of actinolite (fig. 3a), pseudomorphous after augite, set in a groundmass of chlorite, plagioclase, epidote group minerals, and minor sulfide minerals. Many of the actinolite crystals apparently had hollow interiors originally filled with melt, which has now devitrified to chlorite. Actinolite pseudomorphs in this unit also show skeletal, ameboid development. The innermost unit (C) of the chilled margins consists of bladed, subradiating, and skeletal feldspar laths set in a matrix dominated by actinolite, with minor amounts of brown hornblende and magnetite. The plagioclase grains commonly have hollow square cross sections and elongate swallowtail longitudinal sections (fig. 3b).

The elongate and skeletal forms of pyroxene pseudomorphs (now actinolite) and plagioclase from chilled units B and C are similar in form to pyroxene and plagioclase reported from Archean quench metabasalts in Canada (Pearce, 1974; Gélinas and Brooks, 1974), Archean ultramafic lenses in Canada having spinifex textured olivines and quench pyroxenes (Naldrett and Gasparrini, 1971), quenched Proterozoic basalts from the Labrador geosyncline (Pearce and Donaldson, 1974), and modern abyssal basalts (Bryan, 1972).

Experimental studies by Lofgren (1974) indicate that elongate, hollow, and branching plagioclase may be produced by supercooling. The differences in crystal morphology among the three units in the chilled margins of the Deer Lake Complex could therefore be explained by supercooling and concomitant development of a compositional boundary layer at the crystal-melt interface (Lofgren and Donaldson, 1975). Similarly, Drever and Johnston (1972) report that the chilled marginal zone of some olivine dolerite dikes consists of a layer of elongate, branching plagioclase and olivine in contact with a layer dominated by branching pyroxene. It is suggested that rapid cooling, although not a necessity, promoted the development of supercooled conditions near the margins of the Deer Lake sills.

In restricted localities unit C of the basal chilled zone is separated from the overlying peridotite by an additional thin (1-3 m) unit probably related to marginal cooling effects. This unit contains olivine grains less than 1 mm in diameter poikilically enclosed in tremolite, which is pseudomorphous after clinopyroxene. Olivine never composes more than 30

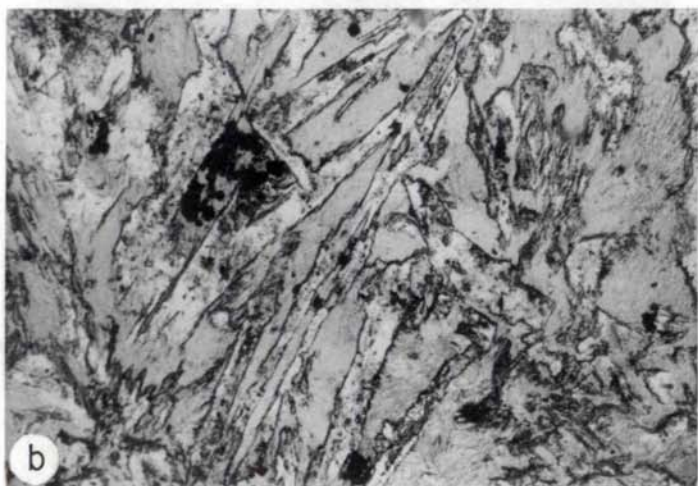


Figure 3 — Microscopic textures of samples from the Deer Lake layered sills. The width of each field is 2.5 mm.

- a) Elongate actinolite grains, pseudomorphous after pyroxene, in chilled unit B. Note hollow interiors of grains in lower right. This texture is thought to result from supercooling promoted by rapid cooling at the sill margin. Sample 14-22, crossed polars.
- b) Skeletal, supercooled plagioclase set in a matrix of actinolite in chilled unit C. Note the hollow, swallowtail sections of the plagioclase. Sample 10-C, plane light.

percent of this zone and thus the rock may be termed an olivine clinopyroxenite. Tremolite and chlorite overgrowths are evident on the outer margins of oikocrysts and also penetrate olivine margins within the oikocrysts. Abundant magnetite, produced by alteration of clinopyroxene, gives the oikocrysts a dark, dusty appearance. Chromite is a minor constituent of the rock.

The sparseness and small grain size of olivine in this unit suggest that olivine crystallization was not initially prolific at the base of the sill. The first formed grains settled only a short distance and may have been chilled due to a downward heat loss.

Peridotite

Peridotite occurs within the Deer Lake Complex as the basal cumulus layers within the differentiated sills. Extensive serpentinization and accompanying magnetite production, together with the development of shear zones as wide as 20 m have virtually destroyed most primary textures. However, primary cumulus textures are locally preserved in unsheared basal units, where rounded, completely serpentinized pseudomorphs of olivine are surrounded by intercumulus clinopyroxene. Less serpentinized areas are rare, but where present reveal fresh olivine kernels (fig. 4a).

Serpentinized olivine composes 55 to 75 percent of the rock (average 65 percent). Equidimensional olivine grains range in size from 1 to 5 mm (average 2 mm) in diameter. Elongate olivine plates, as much as 7 mm long, occur in the lowermost cumulus part of the layered sills.

Single or clustered octahedral grains of chromite, ranging from 0.5 to 1 mm in diameter, never constitute more than 3 percent of any peridotite body. Chromite is a cumulus phase which apparently began to crystallize penecontemporaneously with olivine. Magnetite commonly rims the euhedral chromite grains.

Primary brown hornblende and clinopyroxene are the dominant intercumulus minerals; they may occur together, but more commonly only one of them is present. Both species alter to tremolite and chlorite in various degrees. Hornblende and clinopyroxene oikocrysts generally compose between 25 and 30 percent of the rock.

Clinopyroxenite

Orthopyroxene-bearing clinopyroxenite layers (fig. 4b) consist of subhedral to euhedral cumulus augite (70-85 percent), cumulus orthopyroxene (10-20 percent) now altered to a chlorite-serpentine intergrowth, intercumulus saussuritized plagioclase (3-8 percent), and intercumulus sulfides and oxides (2 percent). Mutual interference textures in some units suggest the development of clinopyroxene overgrowths on early cumulus clinopyroxene. Elongate clinopyroxene grains attain lengths of as much as 4 mm, but most grains do not exceed 0.5 mm. The grains are generally brown and alter to a tremolitic amphibole. Simple twinning along (100) is common in primary, alteration, and overgrowth phases. Orthopyroxene occurs as euhedral cumulus grains ranging in diameter from 2 to 4 mm. Inclusions of clinopyroxene grains within orthopyroxene occur rarely. Rims of plagioclase

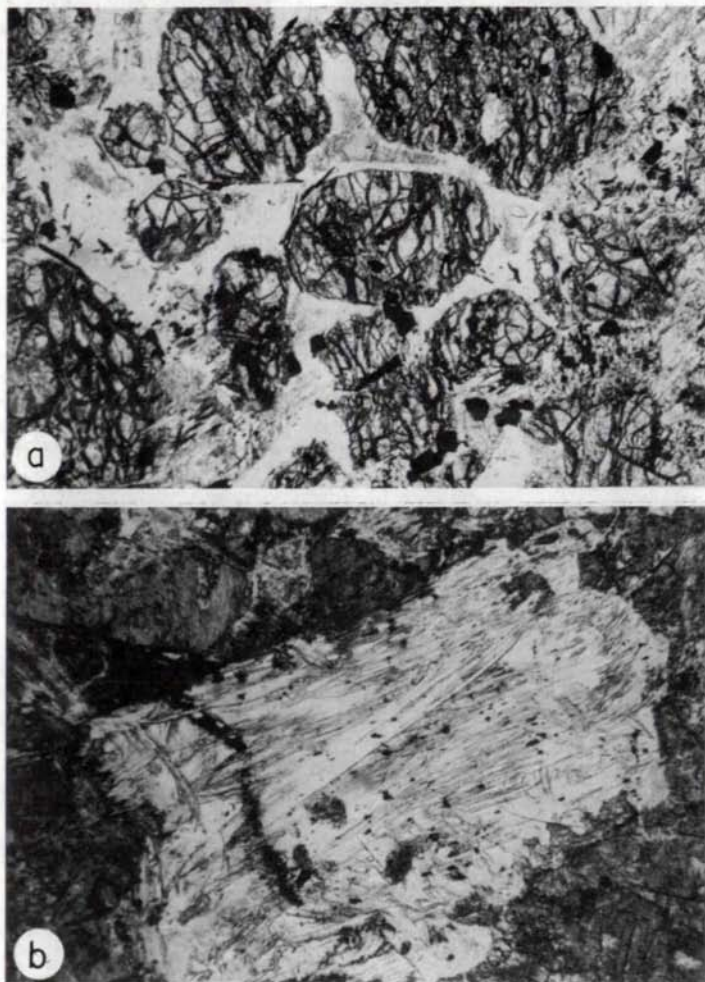


Figure 4 — Microscopic textures of samples from the Deer Lake layered sills. The width of each field is 2.5 mm.

- a) Fresh olivine grains in an amphibole matrix within a peridotite unit. Sample 08-2, plane light.
- b) Clinopyroxenite showing serpentine and chlorite mixture pseudomorphing orthopyroxene (white), surrounded by cumulus grains of euhedral brown augite. Needles within orthopyroxene pseudomorph are actinolite and may represent clinopyroxene lamellae. Intercumulus material is plagioclase. Sample 09-15, plane light.

commonly partly enclose the larger orthopyroxene grains, and possibly represent accumulation of small plagioclase grains trapped by the settling orthopyroxene. The identification of orthopyroxene is based on a combination of form and alteration products because fresh grains are absent. The large grain size, diagnostic chlorite-serpentine alteration, and the occurrence of oriented needles (lamellae) of tremolite-actinolite, possibly pseudomorphous after augite, are criteria used to distinguish orthopyroxene from clinopyroxene. The type of orthopyroxene alteration in the Deer Lake sills is not unlike that developed in altered bronzite from pyroxenite layers in similar sills located near Ely, Minnesota (Schulz and Ripley, 1973; Schulz, 1974).

Porphyritic Gabbro

Clinopyroxenite grades upward into a porphyritic two-pyroxene gabbro that contains plagioclase laths (40-45 percent), relict augite prisms (30-35 percent), poikilitic phenocrysts of tremolitic amphibole after orthopyroxene (15-20 percent), and minor cumulus magnetite (3 percent). Porphyritic gabbro units are characterized by 2- to 3-mm subhedral to euhedral phenocrysts of tremolite after orthopyroxene (fig. 5a), commonly containing small inclusions of plagioclase. The lamellar form of the tremolite, interpreted as reflecting augite exsolution lamellae of the original orthopyroxene, aids in distinguishing this mineral from the smaller, isolated cumulus grains of twinned augite. Highly saussuritized plagioclase laths as much as 2 mm in length constitute another cumulus phase in the rock. In the upper parts of the porphyritic gabbro unit orthopyroxene becomes distinctly subhedral to anhedral and contains greater proportions of plagioclase inclusions. It is possible that this rock type did not form by a cumulus process. The subophitic orthopyroxene phenocrysts represent the latest stages in orthopyroxene crystallization. Intercumulus material is sparse, but where present consists of altered plagioclase, specks of actinolite and chlorite, granular magnetite, and sulfides. Overgrowths on both relict orthopyroxene and augite suggest that adcumulus growth has eliminated much intercumulus liquid.

Nonporphyritic Gabbro

The porphyritic gabbro units are overlain by medium- to coarse-grained hypidiomorphic, nonporphyritic gabbro which shows several unique textural variations. Twinned pyroxene crystals (fig. 5b), or actinolite grains after augite, some as long as 7 mm, compose 35 to 40 percent of the rock, and are surrounded by and intergrown with saussuritized plagioclase laths. Angular grains of optically continuous pyroxene are also commonly poikilitically enclosed by plagioclase. Actinolite pseudomorphs after augite have been observed that completely enclose plagioclase laths, but such occurrences are uncommon. Interstitial intergrowths of sodic plagioclase and quartz occur as constituents of a granophyric variety of the gabbro, whereas in quartz-rich parts of the gabbro interstitial quartz occurs in amounts up to 10 percent. Skeletal ilmenite, commonly altered to leucoxene and rimmed by sphene and biotite, and magnetite normally compose between 8 and 10 percent of all nonporphyritic gabbro units. Apatite is a minor but ubiquitous accessory mineral.

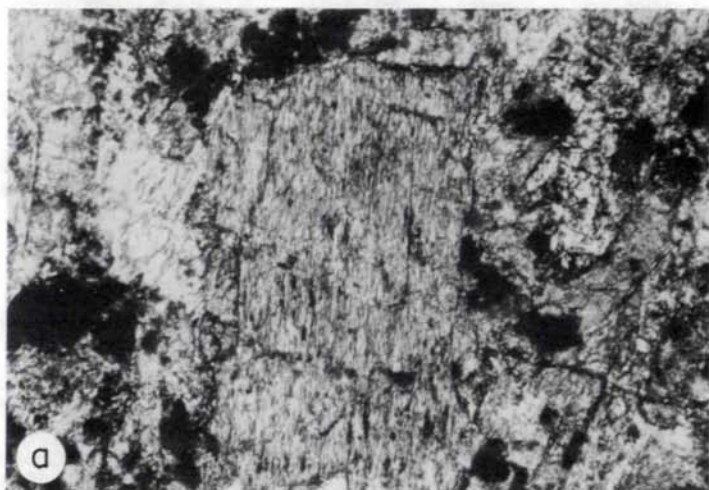


Figure 5 — Microscopic textures of samples from the Deer Lake layered sills. The width of each field is 2.5 mm.

- a) Large pseudomorph of orthopyroxene phenocryst in porphyritic gabbro illustrating lamellar form of tremolite alteration. Bright areas to the left and lower right of the orthopyroxene grain are clinopyroxene, now altered to actinolite. Gray areas are cumulus plagioclase laths. Sample 09-B, crossed polars.
- b) Twinned, prismatic grain of ferroaugite in nonporphyritic gabbro unit. Partial alteration to actinolite can be observed along the margins of the grain. A skeletal grain of magnetite-ilmenite is located in the upper left. Sample 12-2, crossed polars.

Quartz Diorite

Medium-grained felsic rocks, identified mainly from drill core, locally overlie gabbro units. Slender 2-mm laths of altered plagioclase constitute between 50 and 55 percent of the total rock, and recrystallized composite grains of quartz occur in amounts up to 25 percent. Fine-grained amphiboles constitute less than 10 percent of the rock. Pyrite cubes as much as 2 mm in diameter make up 10 to 35 percent of the rock.

Composition of Olivine and Pyroxene

Electron microprobe analyses of selected grains of olivine and pyroxene from the layered sills of the Deer Lake Complex are listed in Table 2. Compositions of fresh olivine in peridotite were determined from both layered sills in the area, whereas pyroxene compositions were determined only for sill 2 (fig. 2).

The compositions of olivine from two samples are Fo_{81} and Fo_{84} .

Table 2 — Electron microprobe analyses of olivines and augites from the Deer Lake layered sills (weight percent).

	1	2	3	4	5	6
SiO ₂	39.70	39.40	53.64	53.86	53.04	49.67
TiO ₂	-	-	0.17	0.12	0.20	0.53
Al ₂ O ₃	-	-	3.34	1.63	3.91	2.74
Cr ₂ O ₃	0.02	0.03	0.82	0.56	0.41	0.01
FeO	15.41	17.70	4.86	5.98	11.47	20.58
MnO	0.33	0.36	0.22	0.28	0.35	0.54
NiO	0.22	0.21	0.06	0.05	0.04	0.02
MgO	44.32	42.00	19.01	15.68	14.37	9.15
CaO	0.24	0.10	18.57	21.26	15.98	17.68
Total	<u>100.24</u>	<u>99.80</u>	<u>100.69</u>	<u>99.42</u>	<u>99.77</u>	<u>100.92</u>
Mg(at)	84	81	54	45	44	27
Fe(at)	16	19	8	10	20	35
Ca(at)			38	45	36	38

1. Olivine, peridotite. Sample 13-9.
2. Olivine, peridotite. Sample 14-13.
3. Augite, peridotite. Sample 14-13.
4. Augite, clinopyroxenite. Sample 16-P.
5. Augite, porphyritic gabbro. Sample 09-B.
6. Ferroaugite, gabbro. Sample 12-2.

These values are within the range for olivine from small layered intrusions reported by Irvine and Findlay (1972), who also noted from empirical evidence that the maximum forsterite content of olivine from layered intrusions is 87 mole percent.

Pyroxene from the sill containing the more forsteritic olivine (sill 2, fig. 2) shows a definite trend toward iron enrichment, ranging from a high magnesium augite in the peridotite unit to a ferroaugite in the nonporphyritic gabbro unit. Similar trends of iron enrichment in pyroxene are common within small, differentiated sills and have been reported by Naldrett and Mason (1968) and Williams and Hallberg (1973) for Archean sills in Canada and Australia respectively.

The importance of olivine and pyroxene compositions in relation to sulfide genesis will be discussed in a later section.

PETROLOGY OF SULFIDE MINERALS IN THE LAYERED SILLS

Description of Sulfide Occurrences

Basal Chilled Margins

Sulfide minerals constitute 0.5 to 4 volume percent of units A and B of basal chilled margins. The total thickness of the sulfide-rich zones rarely exceeds 5 m. The remaining units of the basal chilled margins are virtually barren. Greater amounts of sulfides within the sills are found only in the sporadic patches of felsic cap rocks. The upper chilled margins contain only minor amounts of pyrrhotite. Table 3 shows average sulfide modal analyses.

Table 3 — Generalized summary of sulfide occurrences in the Deer Lake layered sills.

Rock Type	Average Volume Percent Sulfide	Modal Proportions			
		pn	po	cp	py
Quartz diorite	10			5	95
Nonporphyritic gabbro	1			15	85
				25	75
Porphyritic gabbro	0.5-1		10	25	65
			15	25	60
			25	75	
Clinopyroxenite	1		30	70	
Peridotite	0.1-0.2	45	45 ¹	10 ¹	
		70	30 ²		
Chilled unit B	2	11	49	40	
Chilled unit A	2	13	61	26	

Abbreviations: pn, pentlandite; po, pyrrhotite; cp, chalcopyrite; py, pyrite.

¹Intercumulus sulfide

²Inclusion sulfide

Within unit A sulfide minerals occur interstitially to plagioclase and pyroxene (fig. 6a). Contacts between sulfide and silicate grains are sharp, with the sulfides appearing to have been molded about the silicate minerals. Average diameters of sulfide and oxide grains are about 0.1 mm. Pyrrhotite is the dominant sulfide; it generally contains irregular finger-like segregations of pentlandite (fig. 6b). Pentlandite also occupies microfractures within pyrrhotite. These textures suggest that pentlandite exsolved from pyrrhotite during cooling. Chalcopyrite occurs with pyrrhotite as composite grains or as distinct blebs concentrated around the margins of composite grains. It also occurs as individual grains scattered throughout the zone and, rarely, as minute specks completely surrounded by pyrrhotite. The latter textural form suggests that a small amount of chalcopyrite may have exsolved from a pyrrhotite host. Ilmenite commonly occurs as rounded globules within or near the margins of pyrrhotite grains (fig. 6c).

Except for minor differences in abundance and textures, the sulfide-oxide mineralogy is the same for chilled unit B. Chalcopyrite is almost as abundant as pyrrhotite (40 percent) and occurs mainly as distinct disseminated blebs. Ilmenite is nearly twice as abundant in unit B as in unit A and occurs as rounded or spherical blebs. The relationship of ilmenite to pyrrhotite is obscure, for it occurs in distinct clusters rarely in close spatial association with pyrrhotite.

Peridotite

Sulfide phases compose 0.1 to 0.2 volume percent of peridotite units, and have two textural variations: 1) as inclusions within cumulus chromite and olivine grains, and 2) associated with intercumulus minerals. The included sulfide minerals are pentlandite and minor nickeliferous pyrrhotite; they compose 20 percent of the total volume of sulfides present within peridotite units. Within the interstitial material, pyrrhotite and pentlandite--which are nearly equal in amount--and minor chalcopyrite form minute specks and irregularly shaped grains averaging 0.05 mm in diameter. In contrast to the basal chilled margins, anhedral composite grains of sulfide minerals are relatively common in the olivine-rich cumulates. Within the composite sulfide grains pyrrhotite and pentlandite occur, not as intergrowths, but as distinct phases occupying opposite ends of individual sulfide grains. Distinct grains surrounded by magnetite are also common (fig. 6d). Chalcopyrite is a minor constituent of the sulfide assemblage and normally occurs as minute, isolated grains adjacent to the intercumulus pyrrhotite-pentlandite. Primary magnetite occurs only within the composite grains associated with intercumulus minerals.

Clinopyroxenite

Pyrrhotite (30 percent by volume of the sulfides) and chalcopyrite (70 percent) are the only sulfide phases present in these units and normally constitute from 0.5 to 1 percent of the total rock. Chalcopyrite and pyrrhotite generally occur as individual blebs, but rare composite grains were noted. Concentrations of chalcopyrite and pyrrhotite around relict orthopyroxene grains are also common. The sulfides range in size from minute specks to intercumulus grains 0.2 to 0.3 mm in diameter. Primary magnetite forms rare intercumulus blebs together with minor amounts of secondary magnetite produced as a byproduct of pyroxene alteration.

Gabbro

The sulfide mineralogy of the lower parts of the porphyritic gabbro is similar to that observed in the clinopyroxenite units. The middle and upper zones of the porphyritic gabbro units, however, mark the initial appearance of pyrite, Ti-rich magnetite, and ilmenite. Pyrite (60 percent of the sulfide volume), chalcopyrite (25 percent), and pyrrhotite (15 percent) make up the sulfide fraction of the upper porphyritic gabbro units and constitute 0.5 percent of the rock. Pyrrhotite and most of the chalcopyrite occur as isolated intercumulus phases ranging in size from minute particles to grains 0.1 mm in diameter. Pyrite, averaging 0.3 mm in diameter, occurs as euhedral cubes, subhedral grains with ragged boundaries, and as veinlets. Intergrowths of pyrite and silicate minerals along grain boundaries suggest that reactions involving both sulfide and silicate minerals have occurred. Minor amounts of chalcopyrite are associated with primary Ti-bearing oxide phases. Composite grains of ilmenite or titaniferous magnetite, pyrite, and chalcopyrite are relatively common (fig. 6e). Magnetite is present in two forms in the upper parts of porphyritic gabbro units, as small blebs and as larger cumulus grains. Small blebs, similar in form and probably related to the pyrrhotite and chalcopyrite, fill interstices between cumulus phases; bleb-like, rounded magnetite is also a component of composite sulfide-oxide intergrowths. Larger grains of cumulus, subhedral to euhedral magnetite, averaging 1 mm in diameter and containing abundant exsolved ilmenite, make up as much as 3 volume percent of the units. In some areas, regularly spaced, parallel laths of ilmenite occur with amphibole and define an octahedral outline. The texture suggests that magnetite has been dissolved from the oxide phase and replaced by hydrous silicate minerals. It is possible that the solutions responsible for the hydration of pyroxene in the porphyritic gabbro were also responsible for the removal of magnetite from the oxide grains (Davidson and Wyllie, 1968). Ilmenite has resisted major alteration, but has in places been converted to leucoxene.

Nonporphyritic gabbro units have greater amounts of pyrite and Ti-bearing oxides than the porphyritic gabbro units. Minor amounts of chalcopyrite occur with pyrite, mainly within sulfide-oxide intergrowths, and the two constitute 1 percent of the total rock volume. Pyrite also occurs as distinct cubes or as incomplete, ragged crystals. Small pyrite veinlets are uncommon. Grain size of pyrite ranges from 0.3 to 1.0 mm. Magnetite and ilmenite constitute as much as 10 percent by volume of nonporphyritic gabbro units. Textures are similar to those in upper porphyritic gabbro units.

Quartz Diorite

Sulfides are abundant in the late quartz diorite cap rocks and attain concentrations of as much as 35 percent over a few centimeters of drill core; average sulfide concentrations, however, are on the order of 10 percent. Pyrite is the dominant sulfide phase and occurs either as a net of coalescing cubes or as clusters of individual cubes (fig. 6f). Individual pyrite grains average 0.5 mm in diameter and have maximum widths of 2 mm. Oxides are absent.

Upper Chilled Margins

Although the upper and lower chilled margins are essentially identical in silicate mineralogy, the upper chilled margins contain only minor amounts of disseminated pyrrhotite.

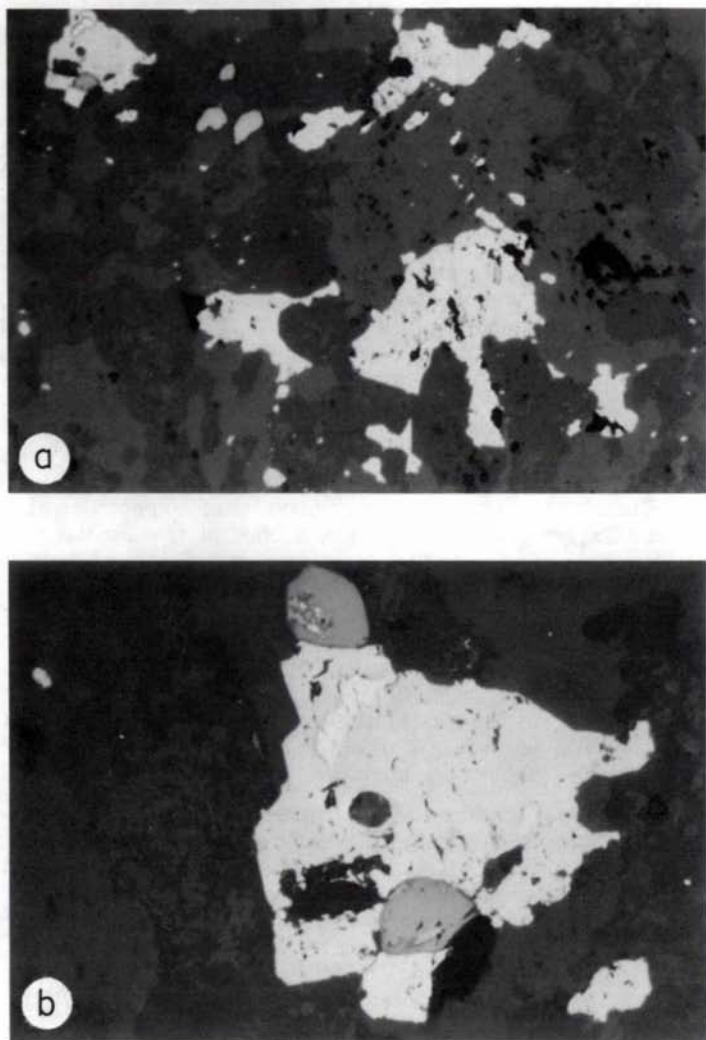


Figure 6 — Microscopic textures of sulfide and oxide minerals from the Deer Lake sills. Polished sections.

- a) Typical occurrence of interstitial sulfides within chilled unit A. White is pyrrhotite, light gray is ilmenite. Sample OC-16-3, plane light. Width of field is 1.5 mm.
- b) Interstitial grain of pyrrhotite (medium gray) with exsolved pentlandite (white). Dark-gray rounded grains near the margins of the pyrrhotite are ilmenite. Sample OC-16-3, plane light. Width of field is 0.375 mm.

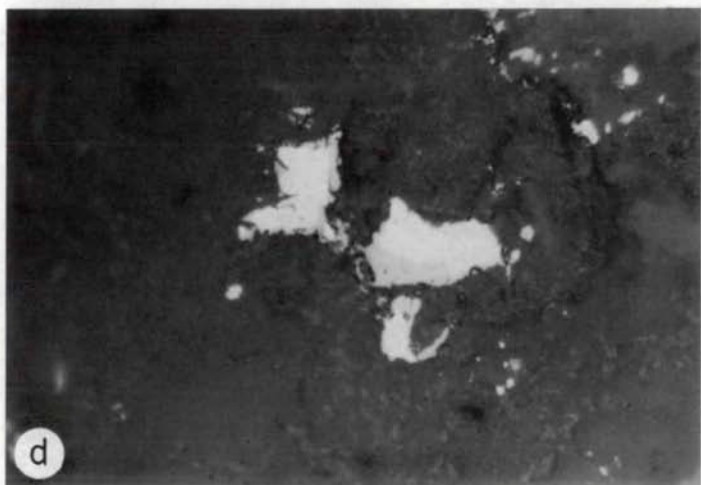
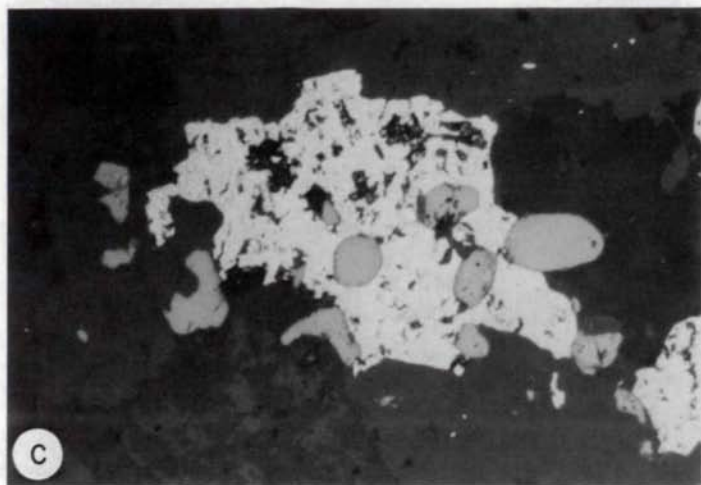


Figure 6 — continued.

- c) Rounded grains of ilmenite (gray) within pyrrhotite (white) from chilled unit A. Sample 3-CD-1, plane light. Width of field is 0.375 mm.
- d) Pentlandite and pyrrhotite grains rimmed by magnetite from a peridotite unit. Sample 13-9, plane light. Width of field is 0.375 mm.

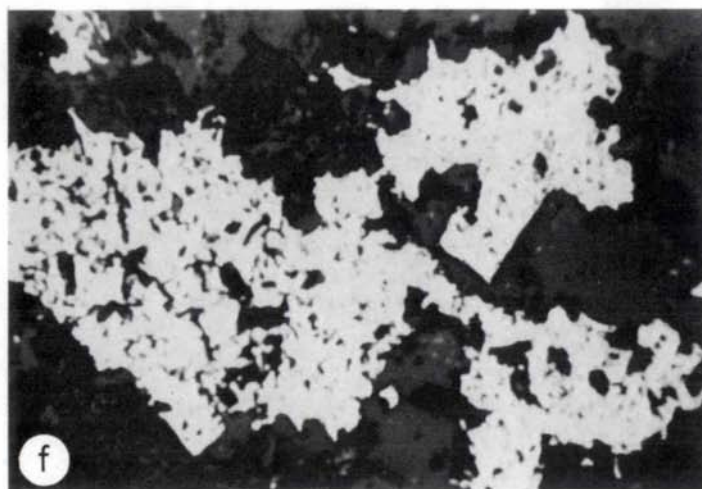
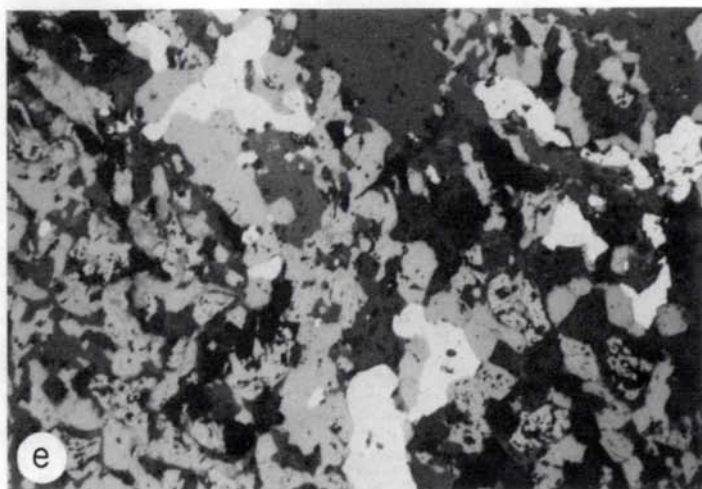


Figure 6 — continued.

- e) Composite grain of ilmenite (light gray), magnetite (dark gray), and pyrite (white) in an upper porphyritic gabbro unit. Sample 08-24E, plane light. Width of field is 0.8 mm.
- f) Pyrite (white) replacing primary silicate phases within quartz diorite cap rock. Sample 03-37, plane light. Width of field is 1.5 mm.

Distribution of Sulfide Minerals

The sulfide minerals in the basal chilled margins appear to be both texturally and mineralogically different from sulfides in the main layered parts of the sills. Approximately 7 m of chilled rock devoid of sulfides separates the basal units that contain sulfide phases from the sulfide-bearing peridotite. In addition, there is a systematic variation in sulfide mineralogy throughout the main layered sequences within the Deer Lake sills. (See Table 3.) Ni-rich minerals occur within the peridotite units, whereas Cu-rich minerals are concentrated in the central parts, and the Fe-, S-rich minerals predominate in the uppermost gabbroic and felsic parts. These observations suggest that two major stages of sulfide generation may have been important in producing the sulfide assemblages at Deer Lake. For these reasons, the petrologic evaluations of the sulfide minerals present in the basal chilled margins and main layered sequences are discussed separately below.

Petrologic Implications of Sulfide Minerals in the Basal Chilled Margins

The presence of disseminated chalcopyrite and pyrrhotite in the basal chilled margins suggests that the sulfides were integral components of the magma that produced the Deer Lake sills. The interstitial textures suggest that the sulfide phases in the basal chilled margins formed from an immiscible sulfide liquid. Field studies by Chamberlain (1967), Naldrett and Kullerud (1967), Nesbitt (1971), and Skinner and Peck (1969) and recent experimental studies by MacLean (1969), Naldrett (1969), and Haughton and others (1974) emphasize the importance of liquid immiscibility in the formation of Cu-Ni sulfides associated with mafic-ultramafic rocks.

Each of the above mentioned studies has pointed out the common association of sulfide minerals with magnetite. Naldrett (1969) has described distinct magnetite bands from the Sudbury District that are thought to have formed from residual liquids which separated from an immiscible sulfide-oxide liquid and has demonstrated that most immiscible liquids that produce Cu-Ni ores are sulfide-oxide liquids. The increase in magnetite content through the ore zone at Kambalda (Ewers and Hudson, 1972) is attributed to precipitation from a residual oxide-rich liquid. At Deer Lake, however, the presence of rounded ilmenite blebs, commonly spatially associated with sulfide minerals, is somewhat perplexing. The texture of the ilmenite grains resembles that expected from crystallization of an immiscible liquid. However, the partitioning of Ti into an immiscible oxide liquid has not been documented. Empirical evidence (Hawley, 1962; Skinner and Peck, 1969) strongly suggests that Ti is partitioned into the coexisting silicate liquid. Naldrett (1969) has suggested that small, sulfide-oxide droplets dispersed in a magma can rapidly lose their oxygen to the enclosing silicate melt. Some of this oxygen may combine with Ti from the silicate magma to form ilmenite. Rounded ilmenite grains associated with sulfides at Sudbury are thought to have originated in such a manner (Naldrett, written commun., 1977), and similar circumstances may account for the origin of ilmenite in the chilled zones of the Deer Lake sills.

The sulfide phases from the basal chilled margins can be treated in terms of the (Fe+Ni)-Cu-S system (Kullerud and others, 1969). The average composition of the sulfide liquid (tbl. 4) was estimated using the composition

of the sulfide minerals present in the chilled units (tbl. 5) and the modal proportions of the minerals present (tbl. 3). In Figure 7a, the bulk compositions of sulfides from chilled units A and B are plotted on a (Fe+Ni)-Cu-S projection in the Fe-Ni-Cu-S tetrahedron. Experimental studies by Kullerud and others (1969) indicate that at temperatures of 1100^o-1000^oC the bulk compositions fall within a two-phase volume that surrounds a pyrrhotite solid solution (po_{ss}--also known as monosulfide solid solution). The trend of the tieline between the compositions of units A and B and the po_{ss} volume suggests that the sulfides in the basal chilled margins represent a mixture of a po_{ss} and a coexisting Cu-rich liquid. It appears reasonable

Table 4 — Average compositions of sulfide phases from the chilled margins and of inclusion sulfides from peridotite of the Deer Lake layered sills

	<u>Fe</u>	<u>Ni</u>	<u>Cu</u>	<u>S</u>
Peridotite inclusion sulfides ¹	37.9	28.5	-	32.7
Chilled unit B	45.9	3.1	13.6	37.4
Chilled unit A	50.5	3.5	8.7	37.3

¹The Co content of the sulfides has been apportioned between Fe and Ni.

Table 5 — Electron microprobe analyses of sulfide minerals from the Deer Lake layered sills (weight percent).

	1	2	3	4	5	6	7	8	9	10
Fe	60.60	61.51	59.27	30.45	40.70	28.93	47.53	30.29	31.18	46.60
Ni	0.03	0.07	0.19	0.01	26.20	29.75	14.19	5.55	0.03	-
Cu	0.03	0.17	0.75	32.54	0.80	0.01	-	29.60	36.06	-
Co	-	0.03	-	0.08	-	6.95	6.37	1.83	0.10	0.10
S	39.29	38.22	39.65	35.85	32.30	33.03	31.93	32.73	32.63	53.70
Total	99.95	100.00	99.86	98.93	100.00	98.67	100.02	100.00	100.00	100.40

1. Pyrrhotite, chilled unit A. Sample 3CD-1.
2. Pyrrhotite, chilled unit A. Sample 16-3-1.
3. Pyrrhotite, chilled unit B. Sample HDFG.
4. Chalcopyrite, chilled unit B. Sample 16-2.
5. Pentlandite, chilled unit A. Sample 16-3-2.
6. Pentlandite, inclusion sulfide, peridotite. Sample 13-9-1.
7. Ni-rich pyrrhotite, inclusion sulfide, peridotite. Sample 13-9-3.
8. Chalcopyrite, peridotite. Sample 13-9-4.
9. Chalcopyrite, clinopyroxenite. Sample 15-09.
10. Pyrite, nonporphyritic gabbro. Sample 12-2.

that pyrrhotite in the chilled margins represents the original po_{ss} that was in equilibrium with the Cu-rich liquid. The small blebs of chalcocopyrite found within pyrrhotite may represent exsolution of Cu contained in the po_{ss} . Distinct chalcocopyrite present in the basal chilled zones is thought to represent the crystallization product of the Cu-rich liquid.

The presence of distinct grains representing the Cu-rich liquid (cp) and the pyrrhotite solid solution (po) suggests that these two phases were physically separated prior to crystallization. Craig and Kullerud (1969) suggested that chalcocopyrite veins and segregations found in the vicinity of

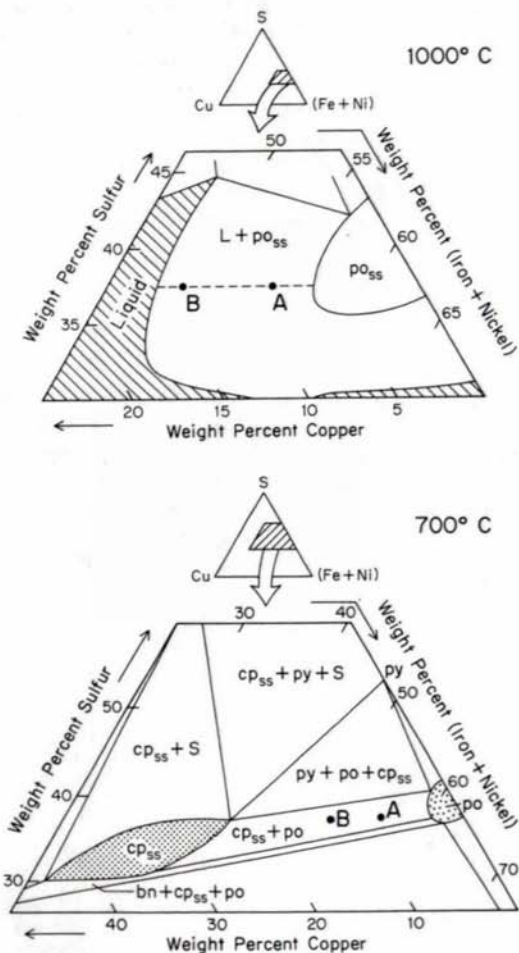


Figure 7 — Bulk compositions of sulfide minerals in chilled unit A (point A) and chilled unit B (point B) on (Fe+Ni)-Cu-S projections in the Fe-Ni-Cu-S tetrahedron. Phase relations in the Fe-Cu-S system: a) at 1000° C, and b) at 700° C. After Kullerud and others (1969).

magmatic Cu-Ni deposits may form at temperatures greater than 850°C from a sulfide liquid that separated from pyrrhotite. Below 850°C, a Cu-rich liquid may not segregate from material with bulk compositions represented by those of Deer Lake chilled margin sulfides. Phase relations at 700°C (Kullerud and others, 1969; fig. 7b) indicate that the bulk compositions of sulfides in the basal chilled margins of the Deer Lake intrusions correspond to mixtures of chalcopyrite and pyrrhotite at that temperature.

It should be noted that although the po_{ss} is not capable of dissolving large amounts of Cu, it can accommodate substantial amounts of Ni. Naldrett and others (1967) have shown that pyrrhotite can accommodate in excess of 15 percent Ni into solid solution at temperatures as low as 300°C. Thus it is not necessary to call upon a fractionated Ni-rich liquid to explain the occurrence of exsolved pentlandite within pyrrhotite in the sulfides of the basal chilled margins of the Deer Lake sills. Naldrett and others (1967) have also shown that the maximum temperature at which chalcopyrite and pentlandite can exsolve together from pyrrhotite is 575°C. Although both phases have been observed as exsolution intergrowths within pyrrhotite, the two never occur as exsolution features within the same grain. Judged from the (Fe+Cu)-Ni-S bulk composition of unit A, it is believed that pentlandite exsolution from pyrrhotite commenced around 350°C (fig. 8) and continued until the Ni-content of pyrrhotite reached its present value of approximately 0.1 percent.

The increase in volume percent of chalcopyrite in chilled unit B over that in unit A is difficult to explain. Textural evidence suggests that a Ni-bearing po_{ss} and a Cu-rich sulfide liquid existed in the basal parts of the magma body that produced the Deer Lake sills. It is possible that crystals of po_{ss} crystallized interstitially to the silicate phases of unit A, and lesser amounts of segregated Cu-sulfide liquid were trapped by the po_{ss} and silicates. The relative increase in chalcopyrite within unit B may indicate that more of the Cu-rich liquid, by virtue of its lower crystallization temperature, was forced--or squeezed--into the overlying zone.

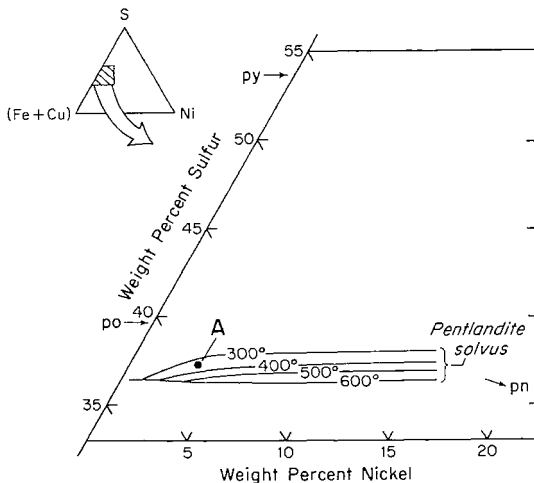


Figure 8 — Portion of the Ni-Fe-S phase diagram (after Naldrett and others, 1967) showing average (Fe+Cu)-Ni-S bulk composition of sulfide phases in Deer Lake chilled unit A (point A).

Manner of Sulfide Accumulation in Basal Chilled Units

Three alternative explanations can be advanced for the occurrence of disseminated sulfides in units A and B of basal chilled margins at Deer Lake:

- 1) Sulfides segregated from the magma and settled to the basal contact under the influence of gravity. This mode of formation assumes segregation and sinking of immiscible sulfide droplets in place.
- 2) Sulfides were produced at chilled margins due to rapid cooling.
- 3) Immiscible sulfide droplets separated prior to or during emplacement of the sill, and because of their density were incorporated only within the basal part of the flowing magma.

The first alternative appears unlikely for two reasons. First, the basal chilled zones did not form by gravity settling, and thus the probability of the sulfides forming in this manner is low. Second, the marginal zones of the sills show textures probably produced by supercooling. If the crystallization was rapid, it is reasonable to assume that the majority of the sulfide liquid was initially present in the basal zones.

Alternatively, as Haughton and others (1974) have demonstrated, a temperature drop can decrease the solubility of sulfur in a mafic magma. However, if rapid cooling were the primary control for sulfide accumulation, comparable volumes and compositions of sulfide minerals would be expected in the upper and lower chilled zones. Immiscible sulfide liquid droplets may have formed in the upper chilled zone along with silicate minerals. Because crystallization temperatures of sulfides are lower than those of pyroxene and plagioclase, the sulfide droplets may have sunk into the magma below. If the magma were unsaturated with respect to sulfur, the sulfide liquid would have dissolved.

The segregation of sulfide droplets prior to or during emplacement (the third alternative) has been called upon by McCall and Leishman (1971) and Nesbitt (1971) to explain the occurrence of massive sulfide bodies at the base of peridotite lenses and sills in Australia. Although the volume of sulfides in the basal zone of the Deer Lake sills is small compared to these massive sulfide bodies, the process of formation may have been similar. Dense immiscible sulfide droplets probably would lag behind during magmatic injection and be incorporated as primary phases only at the base of laterally spreading sills. Because crystallization temperatures of sulfides are lower than those of non-hydrated silicates (Naldrett, 1969), the sulfides could be interstitially molded about the primary silicate minerals.

Petrologic Implications of Sulfides in the Layered Sills

The sulfide minerals present in the layered parts of the Deer Lake sills are thought to have originated from components present within the magma during emplacement and crystallization, and are therefore considered magmatic in origin. The presence of minute sulfide inclusions within grains of cumulus olivine and chromite in peridotite layers suggests that at the time the basaltic magma liquidus was reached the melt contained immiscible liquid sulfide droplets or, possibly, discrete sulfide crystals. There appears to be no other way by which sulfide minerals can form within cumulus grains.

The systematic distribution of sulfide assemblages in the layered sills (tbl. 3) and the relation between sulfide and host rock metal content (tbl. 6) suggest that equilibrium between silicate and sulfide phases was maintained during fractional crystallization. The contact between the Ni-rich and Ni-poor sulfides corresponds with the contact between peridotite and pyroxenite. The average Ni content of the middle and upper clinopyroxenite units and lower porphyritic gabbro units is less than 200 ppm, whereas their Cu content averages nearly 200 ppm. Nickel, which has an affinity for early-forming silicate minerals (regular octahedral sites) and sulfide phases (Burns, 1970), is apparently concentrated in olivine and the sulfide minerals. The early crystallizing pyrrhotite solid solution, however, is not capable of dissolving large amounts of Cu, and because Cu has a preference for distorted octahedral sites (Burns, 1970) it is fractionated in the melt relative to olivine. For these reasons Cu would be concentrated in the units above the peridotite layers. The trend in silicate differentiation, as evidenced by the whole rock Cu-Ni content, has influenced the composition of the sulfides. The fact that these compositional variations are time dependent and did not exist prior to sill emplacement suggests that sulfide phases of changing compositions segregated continually during silicate differentiation and crystallization.

Table 6 — Average Cu-Ni contents through the Deer Lake layered sills (values in ppm).

<u>Rock Type</u>	<u>Number of Analyses</u>	<u>Cu</u>	<u>Ni</u>
Upper chilled units	2	72	67
Quartz diorite	4	78	102
Nonporphyritic gabbro	9	33	37
Porphyritic gabbro			
Upper	6	52	50
Lower	5	163	82
Clinopyroxenite			
Upper	3	252	164
Lower (\approx 3 meters from contact)	6	23	262
Peridotite			
Upper	4	42	1088
Lower	7	44	1368
Olivine clinopyroxenite	5	36	507
Chilled unit C	3	44	71
Chilled unit B	6	98	95
Chilled unit A	8	154	108

A comparison of the distribution of Ni and Fe in coexisting olivine and sulfide from the Deer Lake peridotite units with experimental results reported by Clark and Naldrett (1972) suggests that the Deer Lake sulfide-olivine assemblage is an equilibrium assemblage. Clark and Naldrett equilibrated olivine ($Fe_{0.85}$) with nickeliferous monosulfide solid solution (M_{ss}) at $900^{\circ}C$ and obtained a distribution coefficient (K_D)* of 33.2. Using compositions of olivine and sulfide phases determined from microprobe analyses the calculated K_D for Deer Lake peridotite is 33.0. This similarity is striking, and is further evidence that sulfide-silicate equilibrium was approached in the Deer Lake sills.

The inclusion sulfides in peridotites apparently separated as immiscible sulfide liquids that initially crystallized as Ni-rich po_{ss} . At $1000^{\circ}C$ the bulk composition of the included sulfides plots in the liquid ss region of the Fe-Ni-S system (Kullerud and others, 1969). A liquidus temperature between 900° and $1000^{\circ}C$ is suggested, for at $900^{\circ}C$ the average composition of the sulfides lies within the po_{ss} (M_{ss} of the Fe-Ni-S system)-liquid field (fig. 9a). At 650° the bulk sulfide composition plots within the M_{ss} -(Ni,Fe) $_{3-x}S_2$ stability field (fig. 9b). Kullerud (1963) has shown that pentlandite is not

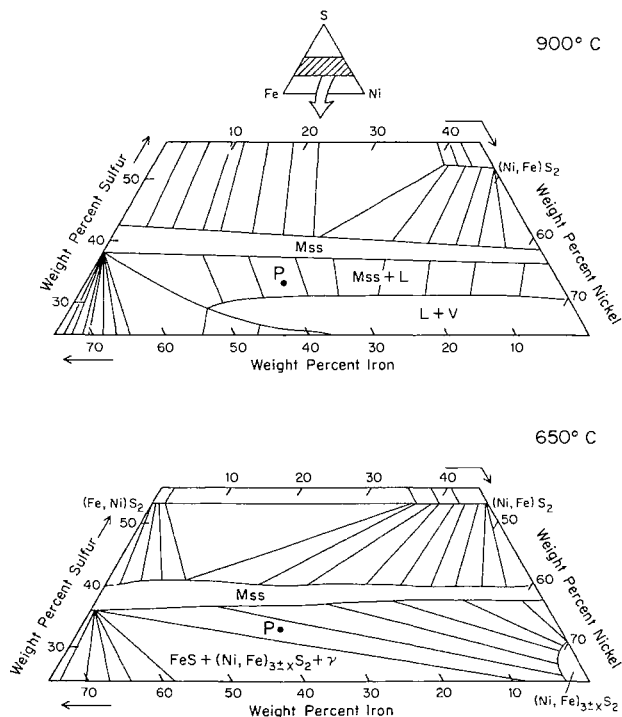


Figure 9 — Phase relations in the Fe-Ni-S system: a) at $900^{\circ}C$, and b) at $650^{\circ}C$. After Kullerud and others (1969). M_{ss} = monosulfide solid solution. Point P refers to the bulk composition of inclusion sulfides in peridotite units.

$$*K_D = \frac{(N_{NiS}/N_{FeS})}{(N_{NiSi_{1/2}O_2}/N_{FeSi_{1/2}O_2})}. \quad N = \text{mole fraction.}$$

stable above 610°C and forms at lower temperatures as a result of reaction between the $(\text{Ni,Fe})_{3-x}\text{S}_2$ phase and the nickeliferous pyrrhotite solid solution (M_{ss}). He also states that pentlandite may form as an exsolution product of the monosulfide solid solution.

There are three methods by which the texturally distinct pyrrhotite-pentlandite assemblages found in peridotite zones could have formed. First, the discrete grains of pentlandite may have formed by complete reaction of $(\text{Ni,Fe})_{3-x}\text{S}_2$ with the monosulfide solid solution. Second, Clark and Naldrett (1972) have shown that subsolidus reaction of sulfides with olivine can produce Ni-rich phases. Thus, the single phase inclusions of pentlandite and pyrrhotite within olivine are possibly the result of an exchange of Fe or Ni between host and inclusion. Page (1970) has called upon this mechanism to explain discrete inclusions of pentlandite and pyrrhotite within olivine in the Stillwater Complex. Because the sulfide grains are extremely small, any changes in Fe-Ni ratio that might have been produced in the olivine host remain undetected. Third, the pentlandite and pyrrhotite intergrowths probably represent the exsolution of pentlandite from the monosulfide solid solution or possibly the exsolution of $(\text{Ni,Fe})_{3-x}\text{S}_2$ which then reacted with M_{ss} to form pentlandite below 610°C.

The occurrence of pyrrhotite and magnetite in the intercumulus material of peridotite units suggests that an immiscible sulfide-oxide liquid separated after the initial sulfide liquid. The coexistence of pyrrhotite and magnetite has been reported from many occurrences where sulfides and oxides are thought to have formed by the separation of an immiscible sulfide-oxide liquid from a mafic magma (e.g., Hawaiian lavas, Skinner and Peck, 1969; massive Ni-sulfides, Naldrett, 1969). The phase assemblage is consistent with results from experimental investigations of the Fe-S-O system reported by Naldrett (1969).

Chalcopyrite and pyrrhotite grains that are molded about cumulus minerals and completely fill interstices in pyroxenite and lower gabbro could have formed from immiscible droplets that accumulated concurrently with pyroxene and plagioclase. Blebs of chalcopyrite localized around large orthopyroxene grains could also indicate that a sulfide liquid was trapped by settling orthopyroxene crystals. The presence of discrete chalcopyrite and magnetite grains indicates that distinct, immiscible oxide and Cu-rich sulfide liquids may have existed in these units.

The close spatial relationships of pyrite and chalcopyrite to titaniferous magnetite and ilmenite in upper porphyritic and nonporphyritic gabbro suggest that such associations probably represent equilibrium assemblages. Irregular, interstitial composite pyrite-chalcopyrite-magnetite-ilmenite grains could have formed from an immiscible sulfide-oxide liquid, with Ti for the first time entering the oxide liquid. However, the unlikelihood of Ti being partitioned into an immiscible sulfide-oxide liquid strongly suggests that the minerals formed directly from the silicate magma. Below the upper porphyritic gabbro unit pyrrhotite was the only stable Fe-sulfide and formed together with Ti-poor magnetite. Above this unit the activity of oxygen within the silicate magma may have increased to the point where magnetite crystallized directly. The crystallization of magnetite would deplete the magma in Fe^{2+} which, coupled with the buildup of sulfur in the residual silicate liquid, could force the precipitation of pyrite and magnetite rather than pyrrhotite.

Irregular grain boundary intergrowths of pyrite and silicate minerals in the nonporphyritic gabbro units and quartz diorite cap rocks suggest that replacement of silicate minerals by sulfides took place. Pyrite may have formed by the reaction of Fe^{2+} -bearing silicate phases with a residual fluid enriched in volatile phases, including sulfur.

In summary, there is evidence that sulfides in peridotite, clinopyroxene, and lower porphyritic gabbro units have developed from immiscible sulfide-oxide liquids which segregated continuously during fractional crystallization. Systematic variations in whole rock metal contents and sulfide mineralogy suggest that equilibrium between sulfide and silicate phases was approached in each unit.

Sulfides in the upper levels of the Deer Lake layered sills probably crystallized directly from the silicate magma. The precipitation of Ti-rich magnetite plus pyrite from the silicate melt may have occurred because of an increased activity of oxygen and competition for Fe^{2+} between sulfide and oxide minerals. Textural evidence suggests that pyrite in some upper gabbro units and in the quartz diorite cap rocks replaced silicate minerals, probably in response to the activity of a volatile-rich residual liquid.

Factors Inhibiting Formation of Cu-Ni Ores in the Deer Lake Complex

Recent experimental studies by Haughton and others (1974) and Shima and Naldrett (1975) have indicated that f_{O_2} , f_{S_2} , temperature, and melt composition are the principal controls on the solubility of sulfur in a mafic magma. The predominant compositional control is the content of Fe^{2+} in the magma. Assuming a constant $f_{\text{S}_2}/f_{\text{O}_2}$ ratio, which Haughton and others (1974) consider likely as the quantities tend to vary sympathetically, a decrease in temperature of 100°C can decrease sulfur solubility by 5 to 7 times. It should be noted that each of these parameters will vary as a magma crystallizes. For this reason evaluation of the relative importance of each variable on sulfur solubility is difficult.

The lack of Ni-sulfide ore occurrences in the Deer Lake sills may be principally a result of a relatively high content of FeO in the melt and iron enrichment of the residual liquid during fractional crystallization. The forsterite content of olivine may be used as a potential ore guide, considering that forsterite content of olivines from lenses and sills that are mineralized is generally greater than Fo_{90} (Naldrett and Gasparrini, 1971). Such olivine compositions are taken to indicate relatively MgO-rich parent melts. Olivine at Deer Lake has a composition of Fo_{81-84} (See Table 2 and Berkley and Himmelberg, 1978.), suggesting a relatively low MgO-high FeO content in the parent magmas of the Deer Lake sills. Small amounts of immiscible liquids apparently separated prior to or during emplacement, but the FeO content and temperature must have been sufficiently high that large amounts of sulfide liquid could not separate. With cooling the residual liquid became even more FeO-rich as indicated by the trend in pyroxene crystallization, and most of the sulfur remained soluble in the magma. Only trace amounts of sulfide liquid separated, as shown by the small amounts of sulfide minerals found throughout the different units of the sills. When the liquid became FeO-poor after crystallization of most of the Fe-silicates and Fe-oxides, sulfur was free to separate from the melt. At this time sulfur

may have been concentrated in a volatile-enriched, probably aqueous phase, which reacted with late Fe-rich silicate minerals to form pyrite. Enough sulfur is present in the upper quartz diorites that if the original magma had been more MgO-rich, small accumulations of massive Cu-Ni sulfides could have formed.

CONCLUSIONS

The principal conclusions are as follows:

- 1) Textural evidence and phase relations suggest that disseminated sulfide minerals (pyrrhotite, pentlandite, chalcopyrite) within basal chilled margins formed from an immiscible sulfide liquid. Bulk sulfide compositions suggest that the chilled margin sulfides represent a mixture of Ni-bearing pyrrhotite solid solution (now pyrrhotite) and a coexisting Cu-rich liquid (now chalcopyrite).
- 2) The immiscible sulfide liquid is thought to have segregated from the magma prior to or soon after emplacement. If the sulfide liquid separated from the melt prior to intrusion, its greater density could have caused its incorporation only in the basal portion of the injected magma. Alternatively, rapid cooling near sill margins could have forced separation of immiscible sulfide droplets from an initially sulfur-undersaturated melt.
- 3) The sulfide minerals in the main layered parts of the sills are Ni-rich in peridotite units, Cu-rich in pyroxenite and lower gabbro units, and Fe- and S-rich in upper gabbro and quartz diorite units. The mineralogical changes are in accord with variations in Cu and Ni whole-rock contents. Sulfide minerals of changing compositions formed during sill differentiation.
- 4) Sulfide minerals in peridotite, pyroxenite, and lower porphyritic gabbro units probably formed from immiscible sulfide liquids. Intergrowths of pyrite, chalcopyrite, magnetite, and ilmenite in upper porphyritic gabbro and nonporphyritic gabbro units probably formed directly from the silicate-rich melt. Some pyrite in upper gabbro and quartz diorite units may have formed by the reaction of a residual sulfur-rich fluid with Fe²⁺-bearing silicates.
- 5) The relatively low MgO content of the parent magma, together with Fe enrichment during differentiation, prevented the early separation of large amounts of sulfide liquid. Consequently, economic concentrations of Ni-sulfides are not present in the Deer Lake sills. Residual sulfur which accumulated in the silicate magma may be represented by sporadic pyrite concentrations in quartz diorite cap rocks.

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