## SULFIDE MINERALOGY AND CHEMICAL EVOLUTION OF THE BABBITT Cu-Ni DEPOSIT, DULUTH COMPLEX, MINNESOTA

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## ABSTRACT

The Babbitt Cu-Ni deposit is one of several, located within troctolitic and noritic rocks of the Duluth Complex, in Minnesota. Sulfide mineralization at Babbitt is somewhat erratically distributed, but two major sulfide zones are identifiable. Basal mineralization occurs near the lower contact with metasedimentary rocks of the Virginia Formation, whereas cloud-zone mineralization is found 150 to 200 m higher in the sequence. Xenoliths of country rocks tend to be abundant within cloud zones. Mineralization is typically disseminated, with sulfide-volume percentages ranging from less than 1 to  $\sim$  30. Massive mineralization occurs rarely, but is most common within a spatially restricted region of the basal zone where host rocks include both igneous and metasedimentary material. Sulfide assemblages consist of pyrrhotite, cubanite, chalcopyrite, pentlandite, and minor amounts of troilite, sphalerite, and bornite. The ratio of cubanite to chalcopyrite increases with sulfide-volume percentage and depth. Sulfide mineralization at Babbitt is copper-rich, with Cu/Ni ratio ranging from 4 to 8. Trends in pyrrhotite, pentlandite, olivine, and orthopyroxene composition are discernible throughout the basal zone and lower cloud-zone mineralization. Nickel content in both pentlandite and olivine tends to vary with pentlandite abundance in the sulfide assemblage. The ratio of the distribution of Ni and Fe between sulfides and olivine i.e., (NiS/FeS)<sub>sulf</sub>/(NiO/FeO)<sub>ol</sub>, is extremely variable, ranging from 2.6 to 39.6. Compositional characteristics of the deposit may be explained by the metal content of the magma, the ratio of silicate to immiscible sulfide liquid, fractional crystallization, and local equilibration of sulfides with mafic silicates.

Keywords: Duluth Complex, Babbitt Cu-Ni deposit, sulfide genesis, compositional variations, Minnesota.

### SOMMAIRE

Le gîte Cu-Ni de Babbitt est situé, avec plusieurs autres, dans les roches troctolitiques et noritiques du complexe massif de Duluth, au Minnesota. La minéralisation en sulfures y est quelque peu erratique, mais on peut identifier deux zones principales de sulfures. La minéralisation à la base se présente près du contact inférieur avec les roches métasédimentaires de la formation Virginia, tandis que la minéralisation en "zone nuageuse" se trouve de 150 à 200 m plus haut dans la série. L'abondance de xénolithes dans les roches encaissantes tend à augmenter dans ces "zones nuageuses". La minéralisation est typiquement disséminée; le pourcentage volumique de sulfure varie de 1 à  $\sim$  30. La minéralisation massive se présente rarement, et le plus souvent dans une région bien délimitée de la zone de base où les roches-hôtes incluent à la fois des sections ignées et des sections métasédimentaires. Les assemblages de sulfures consistent en pyrrhotine, cubanite, chalcopyrite, pentlandite, avec, en moindres quantités: troilite, blende et bornite. Le rapport de cubanite à chalcopyrite croît avec la profondeur et le pourcentage en volume de sulfure. La minéralisation en sulfures est riche en cuivre, avec le rapport Cu/Ni variant de 4 à 8. On peut discerner, dans la minéralisation de la zone de base et de la partie inférieure de la "zone nuageuse", certaines tendances dans la composition de pyrrhotine, pentlandite, olivine et orthopyroxène. La teneur en nickel de la pentlandite et de l'olivine a tendance à varier avec l'abondance de la pentlandite dans l'assemblage des sulfures. Le rapport de la distribution de Ni et Fe entre sulfures et olivine, c'est-à-dire (NiS/FeS)<sub>sulf</sub>/(NiO/FeO),<sub>ol</sub>, varie de 2.6 à 39.6. Les caractéristiques de la composition du gîte peuvent s'expliquer en fonction de la teneur en métaux du magma, du rapport silicate à sulfure immiscible liquide, de la cristallisation fractionnée et de l'équilibration locale des sulfures avec silicates mafiques.

(Traduit par la Rédaction)

*Mots-clés:* complexe de Duluth, gîte Cu-Ni de Babbitt, genèse des sulfures, variations de composition, Minnesota.

#### INTRODUCTION

Several low-grade Cu-Ni deposits are located within mafic rocks of the Precambrian Duluth Complex (Figs. 1, 2). These occurrences are generally included in a class known as flood-basalt-related Cu-Ni deposits (Naldrett 1981). Several studies conducted during the past ten years have dealt with the genesis of sulfide mineralization in the Complex (e.g., Boucher 1975, Weiblen & Morey 1976, Mainwaring & Naldrett 1977, Matlack 1980, Bonnichsen et al. 1981, Ripley 1981, Rao & Ripley 1983, Tyson & Chang 1984, Pasteris 1984, 1985, Foose & Weiblen, in press). Virtually all of these studies have emphasized the role of contamination by country rocks in sulfide formation. The deposits are generally found in the lower portions of troctolitic or noritic sequences near the contact with underlying metasedimentary rocks of Middle Precambrian age. Even at the Spruce deposit (Fig. 2), where immediate footwall rocks are those of the Early Precambrian Giants Range Massif, abundant xenoliths of metasedimentary rocks are found. Although petro-



FIG. 1. Generalized bedrock geology of Minnesota (after Cooper et al. 1981) showing location of the Hoyt Lakes – Kawishiwi area.



FIG. 2. Regional geological setting of the Babbitt, Dunka Road, Spruce, and Water Hen Cu–Ni deposits, Duluth Complex, Minnesota (modified from Cooper *et al.* 1981).



FIG. 3. Cross section showing locations of principal Cu-sulfide-bearing units, line 3600 E, Babbitt deposit.



FIG. 4. Plan map of the 1700 level, Babbitt deposit, showing Cu distribution and cubanite percentages.

logical and geochemical studies have shown rather conclusively that sulfur from country rocks is crucial for ore genesis, many questions remain unanswered concerning the timing of sulfide saturation and the genetic relationship between various sulfidebearing zones in the Complex.

The Babbitt deposit (Fig. 2) is one of the larger in the Duluth Complex, and has been studied extensively by geologists of AMAX Exploration, Inc. Several styles of sulfide mineralization are found in the deposit (*e.g.*, Matlack 1980, Pasteris 1984, Tyson & Chang 1984). We have examined in detail a portion of the Babbitt deposit, including the area of highest-grade mineralization. This report summarizes our results concerning the mineralogy, distribution and composition of sulfide occurrences in the Babbitt deposit. Results of isotopic (Ripley & Al-Jassar, in press) and mass-transfer (Alawi 1985) studies are reported elsewhere.

# LOCAL GEOLOGY AND DISTRIBUTION OF SULFIDES

At the Babbitt deposit, footwall material is composed principally of rocks of the Virginia Formation and Biwabik Iron Formation. Pelitic rocks of the Virginia Formation are cordierite – biotite – plagioclase  $\pm$  orthopyroxene  $\pm$  quartz hornfels, with minor amounts of K-feldspar, ilmenite, graphite and sulfides (predominantly pyrrhotite). The thickness of the footwall Virginia Formation varies from



FIG. 5. Summary stratigraphic section showing whole-rock sulfide abundance and mineralogy of the sulfide assemblages, drill hole 136, Babbitt deposit.

10 to 50 m in the area of the Babbitt deposit. The Biwabik Iron Formation underlies the Virginia Formation, but is never found in direct contact with igneous rocks of the Duluth Complex. Inclusions are abundant in some areas of the Babbitt deposit, especially within the area of higher-grade mineralization known as the Local Boy deposit. Xenoliths of the Virginia Formation are most abundant, and are always orthopyroxene-bearing. Lesser amounts of Biwabik Iron Formation, volcanic rocks, and calcsilicate units of the Virginia Formation are also found as xenoliths. Xenoliths range from a few centimetres to several metres in diameter, and may be as abundant as 25 volume % in areas of basal-zone mineralization.

The Babbitt deposit occurs within a mafic sequence known as the Partridge River Intrusion. Several researchers have divided the intrusive sequence into various units. Grant & Molling (1981) and Chalokwu & Grant (1983) have studied two drill cores from the Babbitt deposit and divided the sequence into three major units based on trace element and petrochemical distinctions. Tyson & Chang (1984) studied four drill cores from the deposit and described five units based on textural and modal analyses. Rao & Ripley (1983) divided the Partridge River Intrusion in the area of the Dunka Road deposit (Fig. 2) into three major units based on petrochemical characteristics. In the area of the Babbitt deposit, our studies suggest that heterogeneity is the rule, and that correlation from drill core to drill core is extremely tenuous. What seems to be certain from results of the studies is that the igneous sequence in the area of the Babbitt deposit developed through repeated magmatic pulses. A lack of welldefined trends in mineral chemistry may be due to replenishment and repeated re-equilibration with melt of similar composition. At the same time, repetitive trends in mineralogy and composition may also reflect periodic addition of magma.

Because of the dynamic nature of rift-related igneous activity, many possibilities exist regarding the genetic evolution of sulfide mineralization. At the Babbitt deposit, at least three major zones of sulfide mineralization are present, which may or may not be correlative with the divisions suggested by the researchers mentioned above. To avoid possible ambiguity, we use the distribution of sulfides to subdivide the igneous sequence. This division may be applicable only in the area of the Babbitt deposit that we have studied (Line 3600 E, and drifts on the 1700 level of the deposit: Figs. 3, 4). Our research has included the petrographic investigation of over 300 polished thin sections. Tabulated values of the proportion of sulfides in whole rocks in volume % and of individual minerals in sulfide assemblages from samples collected from several drill-cores are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

Unit I at Babbitt contains what is normally referred to as basal-zone mineralization. In drill core 136, this unit extends from the basal contact (546 m) to a depth of 411 m (Figs. 3, 5). Sulfide mineralization in this unit is both disseminated and massive in form. Areas of high-grade ore containing greater than 4.7% S and 1.0% Cu occur within both norite and hornfels. The distribution of sulfide in this unit is erratic (Fig. 5), with no clear distinction between massive and disseminated ore. The most continuous occurrence of sulfide mineralization, with grades in excess of 1% Cu, has been outlined in the vicinity of 518 m (1700 level, Figs. 3, 4). This area was extensively evaluated by AMAX as part of the Minnamax project. The high-grade ore rests essentially on the contact with the Virginia Formation, and high concentrations of sulfide commonly are found around and within inclusions of hornfels.

TABLE 1. REPRESENTATIVE CONCENTRATIONS OF MINOR ELEMENTS IN SULFIDE MINERALS FROM THE BABBITT DEPOSIT

Depth (m)	Ag	Mn	Zn	Pb	Depth (m)	Ag	Mn	Zn	Pb
	Py	rrhotite			· (	Chalcopy	rite/Cuba	nite	· · · · · · · ·
266.1	63 "	400	467	80	269.1	50	68	350	
275.2	25	70	800		270.6	40	460	48	
278.0	10	183	250	163	273.7	17	187	3790	151
285.9	27	130	1183	10	292.0	121	79	2183	167
298.1	30	160	153		293.5	13	58	1240	92
310.3	21	504	1006	305	299.6	85	167	37	25
315.1	15	349	951	155	299.9	15	146	1250	188
337.7	49	222	833	253	337.7	28	257	5267	190
352.9	10	195	2362	178	371.2	33	110	3662	183
364.2	57		482		371.8	79	106	1130	28
371.8	208	32	350		380.4	113	88		
380.4	140	30	550		396.2	22	112		62
393.8		62	100		415.4	49	92	5900	132
415.4	14	88	833	176	416.0	57	159		
429.1	10	91	278		418.5	4	59		414
441.6	29		414		441.3	69	669	4089	324
445.9	24	154	2916	200	441.6	96			
447.4	113		933		444.4	23		433	
450.8	63		467		447.4	96	63	650	183
455.0	27	165	650		450.8	76	9	32	
458.4	8	164	1458	221	459.6	23	142	4395	193
460.2	31 -	22	321		460.2	39	39	389	
462.7	31	161	1518	255	461.1	28	70	317	20
465.4	38	76	520		465.4	37	32	283	
468.1	33	12	500	12	468.1	80			
473.3	23	70	417		474.2	42	20	267	
477.9	23	97	946	211	477.9	11	117	405	267
481.0	4	96	2770	163	482.5	24	77	691	429
485.5	60	55	431	122	491.6	88	122	583	25
493.1	161	222	2268	412	502.3	49	157		198
503.8	28	103	3650	173	505.3	12	85	291	148
516.3	23	7	283		526.7	2	132		37
529.7	28	80	3260	190	528.2	25	96	2550	165
531.2	10	85	3280	199	529.7	29	100	860	207
534.3	38	100	1300	234	531.2	23	170	709	79
537.3	-4	93	323	154	532.8	302	124	4461	169
544.0	13	100	5140	153	533.1	77	36	510	14
546.5	、 2 <u>1</u>	127	2309	164	535.8	7	99	556	193

Values in ppm. Drill hole 136. - not detected.

Above the basal mineralized unit an overall decrease in proportion of sulfide is encountered. In the depth interval 411 to 353 m, sulfides are sparse, commonly constituting no more than 1 volume % of the igneous host. In drill hole 136, two exceptions to this general distribution occur. A very thin (< 6 cm) occurrence of norite containing 8% sulfide is found at 394 m, and an interval containing up to 10% sulfide is found between 370 and 380 m.

Cloud-zone mineralization (Watowich 1978, Ryan 1984) is designated Unit II and is found between 353 and 257 m. The proportion of sulfide is again variable in this interval, ranging from 0.5 to 58 %. Copper grade is generally less than in the basal zone, averaging between 0.3 and 0.4 weight %.

The interval from 257 m to the surface is designated Unit III, and is characterized by low abundance of sulfides, normally less than 0.5 volume %.

Massive-sulfide mineralization occurs at several localities, but is not spatially extensive. For example, in drill hole 136, only eight intervals with sulfide abundance in excess of 10 volume % are encountered (Table 1). Four of these are within the cloud zone and have a thickness of less than a few centimetres. Massive mineralization is most extensive in the lower portion of the basal mineralized zone, within the interval 528 - 531 m in drill hole 136 (e.g., Figs. 3, 4). Thin intervals of massive mineralization are also found in drill holes 156, 189 and 146 (Fig. 3), all within 3 m of the basal contact.

We stress that the divisions suggested here based on sulfide distribution are not rigid. It is clear that although sulfides are found throughout the bulk of the Duluth Complex, proportions and grade vary erratically. The divisions outlined above provide a convenient frame of reference for our analytical and geochemical studies.

#### SULFIDE TEXTURES

General textural features of sulfide minerals in the Babbitt deposit have been described by Boucher (1975), Tyson (1979), Matlack (1980) and Pasteris (1984). The textural types include massive, intersti-



FIG. 6. Photomicrograph showing sulfides (s), ilmenite (ilm), and biotite (bio) interstitial to plagioclase (pl). Field width is 1.7 mm. Reflected, plane-polarized light.



FIG. 7. Symplectitic intergrowth of sulfides (s) and orthopyroxene (opx) near the margin of a plagioclase grain. Field width is 1.7 mm. Transmitted light, crossed polars.

tial, veins and veinlets, inclusions in or intergrowths with silicates and oxides, and exsolutions. Most of the sulfides at Babbitt are broadly classified as interstitial, but several textural variations may be found within a single sample.

Three types of interstitial sulfides characterize the Babbitt deposit. Sulfide minerals may occur in voids between olivine or orthopyroxene and plagioclase, strongly associated with interstitial biotite and ilmenite (Fig. 6). Less commonly, sulfides occur interstitially to mafic silicates and plagioclase without associated interstitial silicates or oxides. Where the proportion of sulfides is high, particularly near the massive occurrences of the basal zone, a continuous network of sulfide surrounds the silicates. This texture may occur in igneous rocks or Virginia Formation hornfels.

Sulfide veins and veinlets occur on two scales. Veinlets are part of the interstitial mineralization, normally connecting two sulfide masses. The veinlets cross-cut silicate minerals and suggest a late crystallization of sulfides and, in some cases, a second-



FIG. 8. Inclusions of chalcopyrite (s) within a plagioclase (pl) overgrowth. Field width is 1.7 mm. Transmitted light, crossed polars.

ary mobilization. The mineralogy of the veinlets is variable (see below), but tends to be essentially the same as the sulfide grains that they connect. A similar observation has been made by Pasteris (1984). Large scale (metres) veins have been described by Matlack (1980) and Matlack & Watowich (1982) as characteristic of massive mineralization. At Babbitt, the massive mineralization does not show a welldefined lenticular form. It is more accurately described as a series of anastomosing veins in both igneous rocks and footwall hornfels, as proposed by Matlack (1980) and Matlack & Watowich (1982). However, mineralization of this type is confined to very near the footwall contact and does not extend vertically upward or downward as part of a welldefined fracture system.

Sulfide minerals may be intergrown with interstitial silicates. Symplectitic intergrowths with pyroxene and oxides (Fig. 7), as well as simpler intergrowths with biotite, are found. Sulfides may also be included within olivine, orthopyroxene, ilmenite and, more commonly, plagioclase. Inclusions within plagioclase tend to be Cu-rich, and are commonly found along marginal overgrowths (Fig. 8). Silicate alteration tends to be more intense in these areas, compared to the core of the plagioclase. Sulfide inclusions (principally chalcopyrite) in plagioclase overgrowths have been described in several areas of the Complex (Weiblen & Morey 1976, Pasteris 1984: South Kawishiwi intrusion; Ripley 1981: Dunka Road). Weiblen & Morey (1976) and Pasteris (1984) have shown that the Ca content of plagioclase is higher in overgrowths containing included Cu-rich sulfides than in sulfide-free cores. Our analyses of samples from the Babbitt deposit indicate that this trend generally holds, but that more sodic sulfidebearing margins also occur. Figure 9 illustrates the trends observed in three samples from different zones in the Babbitt deposit. An abrupt increase in An content within sulfide-bearing margins on plagioclase is observed for most of the grains, followed by a rapid decrease. A slight increase in An content is also observed within grain margins free of sulfide inclusions. The magnitude of the An increases is depressed relative to that observed in sulfide-bearing margins, and suggests that large shifts in An content are related to the local presence of included sulfide. Although core compositions of plagioclase may be extremely variable (An<sub>53</sub> to An<sub>70</sub>), there appears to be no correlation between core and rim compositions and the presence of sulfide inclusions.

Exsolution features are common in the sulfides, with a variety of lamellar and bleb-like forms observed. Exsolution textures are recognized in all textural types of sulfides mentioned above. Specific exsolution-controlled assemblages are discussed below.

## DISTRIBUTION OF SULFIDE MINERALS

Variations in the proportion and mineralogy of sulfides for drill hole 136 are shown graphically in Figures 5 and 10; tabulated values are available from the Depository of Unpublished Data. Some of the more important aspects of sulfide mineralogy and distribution with respect to genetic evaluation are discussed below.



FIG. 9. Variations in An content through plagioclase grains with and without sulfides included in marginal overgrowths. All plots are for samples from drill hole 136. Sample depths are as follows: plots A-C, 453.5 m; plots D-F, 273.7 m; plots G-J, 371.2 m.

## Pyrrhotite

Within the basal mineralized unit, the concentration of pyrrhotite relative to the entire sulfide assemblage ranges from 10 to 50%. Although anhedral, monomineralic grains do occur, pyrrhotite more commonly is associated with other sulfide phases in both massive and disseminated occurrences. Minor amounts of troilite are intergrown with pyrrhotite throughout the sulfide-bearing intervals. In massive sulfide and higher-grade disseminated ore, pyrrhotite occurs intergrown with cubanite and with lesser amounts of chalcopyrite and pentlandite. Grains of pyrrhotite may be enclosed in cubanite (Fig. 11) or may enclose cubanite and chalcopyrite (Fig. 12). The percentage of cubanite generally exceeds that of pyrrhotite in massive ore-zones, although local areas of massive pyrrhotite are also noted.

In disseminated sulfide zones, or at higher stratigraphic levels in the troctolitic sequence (Units II, III), pyrrhotite ranges from 5 to 90 volume % of the sulfide phase. However, within these zones pyrrhotite is normally far less abundant than cubanite plus chalcopyrite. Pyrrhotite occurs as part of polymineralic interstitial grains, as veinlets, or intergrown with silicates.

## Troilite

Although troilite occurs in most sulfide assemblages in the Babbitt area, its abundance rarely exceeds 5 % of the sulfide phase. It occurs in greatest abundance where total sulfide and cubanite proportions are high. Troilite is found exclusively as irregular lamellae within pyrrhotite grains.

## Cubanite

Cubanite occurs in all sulfide zones, and is the most important Cu-bearing sulfide mineral in the basal mineralized zone. Its abundance varies from 10 to 80 % of the sulfide volume. Cubanite normally occurs as part of a polymineralic mass including pyrrhotite, chalcopyrite and pentlandite. Individual minerals are present in the following ranges: 10-60% pyrrhotite, 20-70% cubanite, 1-10% chalcopyrite, 0-5% pentlandite. Grain boundaries with other sulfides are generally smooth and, in most cases, suggestive of a cogenetic relationship. Cubanite may enclose small grains of both pyrrhotite and pentlandite, flames of pentlandite, and lamellae of chalcopyrite. Cubanite, with or without lamellae of chalcopyrite, is also commonly found enclosed by pyrrhotite. Areas of disseminated mineralization typically exhibit polymineralic grains in which Cusulfides occur near the margin of pyrrhotite grains.

There is a correlation between the chalcopyrite/cubanite ratio in a sample and the volume %



FIG. 10. Detailed stratigraphic section through the lower portion of drill hole 136, showing sulfide mineralogy and volume proportions.

of sulfide present. Figure 13 indicates that at volume proportions in excess of ~6%, cubanite is the predominant copper-bearing sulfide. Pasteris (1984) and Boucher (1975) have suggested that replacement of early-formed pyrrhotite by more Cu-rich minerals has occurred, and that massive cubanite is the result of such a process. However, our studies of both massive and disseminated mineralization suggest that the observed textures may result from fractional crystallization of a sulfide liquid, the attainment of sulfide saturation at varying ratios of silicate magma to sulfide liquid (see below), and equilibration during cooling.

Although phases in the central portion of the system Cu–Fe–S, such as mooihoekite, haycockite and



FIG. 11. Photomicrograph showing cubanite (cb) enclosing grains of pyrrhotite (po). Field width is 0.85 mm. Reflected, plane-polarized light.



FIG. 12. Pyrrhotite (po) enclosing grains of cubanite (cb 1) and a compositionally similar phase (cb 2). Field width is 0.85 mm. Reflected, plane-polarized light.

talnakhite, have not been detected in our study, a mineral that is optically distinct from (but compositionally similar to) cubanite occurs locally. Figure 12 shows the two minerals in direct contact, both enclosed within pyrrhotite. The mineral is always associated with cubanite, but is paler in color and much less anisotropic. Compositional differences between the mineral and cubanite are essentially nondetectable, as discussed below. The observed differences between grains may be a function of optical orientation. However, the magnitude of the differences in physical and optical properties, as well as the scarcity of grains with similar characteristics, do not support such a premise.

## Chalcopyrite

Chalcopyrite is markedly less abundant than cubanite in the basal zone, with sulfide proportion varying between 5 and 20 %. Chalcopyrite normally



FIG. 13. Plot of chalcopyrite/cubanite ratio versus volume % sulfide, Babbitt deposit.

occurs in the massive-sulfide zones as lamellae within cubanite (Fig. 14) or as small blebs dispersed as a halo around larger polymineralic sulfide masses. The abundance of chalcopyrite increases upward. It is more abundant within the disseminated sulfide zones, where it may occur to the total exclusion of cubanite and pentlandite. Within areas containing less than 1 volume % sulfide, chalcopyrite is the predominant Cu-bearing mineral, and commonly exceeds pyrrhotite in abundance. Chalcopyrite occurs either as part of composite grains with pyrrhotite or as independent monomineralic grains. Minor amounts of pentlandite may be found in the composite grains; higher in the troctolitic sequence, bornite may occur with chalcopyrite as an abundant phase formed by exsolution.

## Pentlandite

Pentlandite occurs in all sulfide-bearing zones at Babbitt, but its concentration rarely exceeds 10 % of the total volume of sulfide. Only sporadically (Figs. 5, 10) does pentlandite abundance reach 20 %. Pentlandite occurs as fractured, equidimensional grains within composite sulfide grains or as exsolution flames and lamellae within pyrrhotite and cubanite. In composite clusters of sulfides, pentlandite tends to occur along the outer margin of grains. Discrete grains of pentlandite are rare, but do occur in zones of disseminated sulfide associated with chalcopyrite and pyrrhotite.

#### Bornite

Bornite occurring with chalcopyrite probably formed by exsolution (Fig. 15). Stratigraphically it is first identified with chalcopyrite and cubanite in a sample located 25 m above the basal contact, but is not seen again until  $\sim$  72 m above the contact. At higher stratigraphic levels bornite is almost always found with chalcopyrite in zones of disseminated sulfide. Only rarely does bornite constitute the major portion of a sulfide grain. Intergrowths of chalcopyrite, bornite and pentlandite are also encountered locally.

## Sphalerite

Sphalerite occurs as a prismatic, flame-, or starlike exsolution mineral within cubanite (Fig. 16) and, locally, chalcopyrite. Sphalerite abundance is highest in the basal massive-sulfide zones, but its concentration never exceeds 1 %. Although sphalerite is most abundant in massive zones, it is found in all areas where cubanite concentration is relatively high.



FIG. 14. Photomicrograph showing lamellae of chalcopyrite (cp) within cubanite (cb). Field width is 0.85 mm.



FIG. 15. Composite grain of bornite (bn) and chalcopyrite (cp). Field width is 0.43 mm.

COMPOSITION OF THE SULFIDE MINERALS

Concentrations of major and minor elements present in sulfide assemblages from the basal mineralized zone were determined using a wavelengthdispersion electron microprobe and atomic absorption (AA). Sulfide mineral separates for AA analyses were obtained with a dental drill and digested using a perchloric acid – liquid bromine solvent. Because many of the sulfide minerals from the Babbitt deposit are polymineralic in form, contamination problems in this technique are difficult to detect. However, purity of individual samples is estimated to be > 90 %, and minor-element results are therefore considered instructive. Concentrations of Ag, Mn, Zn and Pb were determined by AA methods, whereas concentrations of Ni, Co, Fe, Cu and S were measured by electron-microprobe techniques.

Results of representative analyses are given in Tables 1 and 2. A complete set of results of 94 electron-microprobe analyses of sulfide minerals through the lower mineralized zones of drill holes



FIG. 16. Grains of exsolved sphalerite (sph) within cubanite (cb). Field width is 0.43 mm.

136 and 156 is available from the Depository of Unpublished Data. Iron content of pyrrhotite varies between 59.5 and 62.2 weight %, whereas Ni never exceeds 0.46%, and averages  $\sim 0.15\%$ . Although pyrrhotite composition varies somewhat erratically, a general pattern with depth is found in drill hole 136 (Fig. 17). The iron content of pyrrhotite fluctuates about a mode of 61 weight % Fe throughout the interval 546 to 442 m. Above this depth through ~ 350 m, Fe content drops to near 60% before again increasing to 61%. The increase in Fe content of pyrrhotite at ~ 350 m coincides closely with the beginning of cloud-zone mineralization. Values from 411 to 350 m are representative of sulfide-poor troctolitic rocks. Minor-element contents of pyrrhotite are also variable, and show no spatial trends or differences between types of sulfide. Relatively high Zn values in several pyrrhotite separates are attributed to sphalerite associated with minor amounts of included chalcopyrite.

Copper contents of chalcopyrite and cubanite vary from 33 to 35.2 and 21.0 to 23.8 weight %, respectively. Cubanite stoichiometry varies between Cu<sub>1.0</sub>Fe<sub>2.1</sub>S<sub>3</sub> and Cu<sub>0.94</sub>Fe<sub>1.9</sub>S<sub>3</sub>. Major- and minorelement compositional zoning within grains is not detected, nor are regular spatial variations within sulfide zones. Silver tends to be enriched in Cu-bearing phases relative to pyrrhotite; concentrations range from 7 to 300 ppm. We have failed to detect significant differences between cubanite and the associated optically distinct phase described above. Table 3 is a partial listing of compositions obtained from a traverse through cubanite and the associated phase shown in Figure 12. There are minor compositional differences between various spots, but the range in compositions shows a complete overlap between the two minerals. Computation of chemical formulae reveal no differences; these fall in the normal range for cubanite.

Pentlandite exhibits the most variable chemical composition, with Fe and Ni contents ranging from 27.4 to 34.3 and 29.3 to 37.4 weight %, respectively. Cobalt is concentrated in pentlandite, and ranges in abundance from 0.6 to 5.0 weight %. Copper content of pentlandite is generally low, but values as high as 3.8% are locally encountered (Table 2). Experimental studies by R. Hill (CSIRO, pers. comm.) indicate that cupriferous pentlandite is not uncommon in low-sulfur systems, such as those which give rise to cubanite-rich assemblages. Spatial variations in the nickel content of pentlandite are similar to those of Fe in pyrrhotite (Fig. 17). In the depth interval 393 to 546 m, the nickel content in pentlandite varies from about 31 to 34 weight %, with most samples near 32 weight %. Between 312 and 380 m, the nickel content of pentlandite increases, before again decreasing at 311 m. The stratigraphic divisions based on the nickel content of pentlandite in general conform to the boundaries established for basal and cloud-zone mineralization, and suggest a possible genetic difference between sulfides in these zones. Nickel content of pentlandite also shows a moderately strong correlation with amount of pentlandite present. Figure 18 shows that the nickel content of pentlandite in basal-zone mineralization is variable in samples where pentlandite abundance is less than or equal to 3 volume % of the sulfide phase. Where pentlandite abundance

<u> </u>			NEODO IN N	LIGHT FERG	<u></u>			T			
				Pyrrhot	ite			Troilite			
Sample Depth (m)	315.1	319.4	380.4	389.2	445.9	531.2	537.3	315.1	445.9	477.9	
Fe	61.27	60.92	61.44	59.75	61.64	61.60	61.33	63.09	63.21	64.13	
Ni	0.01	0.14	0.12	0.46	0.05	0.07	0.18				
S Total	37.68 98.96	39.22 100.28	39.63 101.27	39.74 100.00	37.71 99.40	38.55 100.30	38.46 99.97	36.21 99.30	36.21 99.42	36.67 100.80	
					Atomic	Proportion	ns	1			
Fe Cu Ní	1.097	1.091  0.002	1.100 0.001 0.002	1.070 0.001 0.009	1.104	i.103 0.001 0.001	1.098 	1.130	1.132	1.148	
Co S	1.175	1.223	1.236	1.239	1.176	1.202	1.199	1.129	1.129	1.144	
	1		Pentlandit	e				Cubanite	ubanite		
Sample Depth (m)	319.4	380.4	393.8	531.2	537.3	315.1	319.4	380.4	474.9	497.7	
Fe	29.46	21.98	31.56	33.84	31.69	40.72	41.03	41.65	41.87	40.54	
Ni Co	36.45	39.97 1.84	30.78	31.23	31.49 1.64						
S Total	33.45 100.15	33.07 100.68	33.06 99.71	33.35 100.53	33.40 98.26	35.12 98.45	34.83 98.72	35.36 100.82	34.38 99.10	35.46 100.00	
					Atomic	Proportion	ns				
Fe Cu Ni	0.528	0.394 0.060 0.681	0.565 0.001	0.606 0.001	0.567 0.001	0.729 0.356	0.735 0.355	0.746 0.375	0.750 0.360	0.726 0.375	
Co S	0.013	0.031	0.072	0.034	0.028	1.095	1.086	1.103	1.072	1.106	
			Chalcop	yrite		l		Bornite	Sphale	erite	
Sample Depth (m)	315.1	319.4	380.4	410.9	485.5	531.2	546.5	380.4	531.2	535.8	
Fe Cu Ni	30.87 34.43	30.71 33.47	30.89 34.99	29.79 33.50 0.04	31.40 33.92	30.68 34.38	30.29 33.18 0.08	12.17 61.79	9.37 1.53 0.02	8.77 0.55	
Co Zn S Total	 34.18 98.33	 34.84 99.02	0.09 34.92 100.89	 35.45 98.79	35.54 100.86	 34.53 99.38	35.18 98.73	0.23 26.08 100.27	55.30 34.05 100.27	57.10 33.74 100.16	
					Atomic	Proportion	18	1	ł		
Fe Cu Ni	0.553 0.542	0.550 0.527	0.553 0.551	0.533 0.527 0.001	0.562 0.534	0.550	0.542 0.522 0.001	0.218 0.972	0.168 0.024	0.157 0.009	
Co Zn S	1.066	1.087	0.001 1.089	1.106	1.108	1.077	1.097	0.004 0.813	0.846	0.874 1.052	
								I	L		

TABLE 2. ELECTRON-MICROPROBE ANALYSES OF REPRESENTATIVE SULFIDE MINERALS FROM THE BABBITT DEPOSIT, DRILL HOLE 136. VALUES IN WEIGHT PERCENT.

exceeds  $\sim 3$  %, there is a systematic decrease in the nickel content of pentlandite with increased modal proportion. A similar trend is apparent for the samples in the lower section of Unit II, but is displaced toward higher nickel contents of pentlandite (Fig. 18a).

## OLIVINE-ORTHOPYROXENE COMPOSITIONAL DATA

Nickel contents and Mg/(Mg + Fe) values of olivine and orthopyroxene from basal zone and lower cloud-zone mineralization are given in Table 4 and graphically illustrated in Figure 19. Because of the presence of abundant xenoliths, an uninterrupted igneous sequence could not be sampled. In interpreting the compositional data the possible effects of country-rock contamination must be considered. However, analysis by Alawi (1985) suggests that although some orthopyroxene crystallization was initiated by the addition of SiO<sub>2</sub> from country rocks, transfer of Fe and Mg was minimal. We consider the variations in Fo and En contents to reflect differences in magma composition produced by processes other than contamination. The compositions of olivine and orthopyroxene in the basal mineralized zone at Babbitt vary from Fo<sub>58</sub> to Fo<sub>23</sub> and  $En_{67}$  to  $En_{37}$ , respectively. A distinct break in compositional trends occurs at  $\sim 493$  m, where Fo and En contents decrease dramatically. The orthopyroxene in the norites maintains these values to a depth of 544 m. A thin (2 m) troctolite unit just at the contact between footwall hornfels and igneous material is characterized by olivine and orthopyroxene of much higher Mg-content.

Nickel contents of olivine and orthopyroxene closely parallel variations in Mg content. Nickel values of olivine vary from 0.07 to 0.20 weight % NiO and those of orthopyroxene, from 0.02 to 0.08 %. Of particular note is the correlation between nickel content of olivine and pentlandite, and pentlandite abundance. A plot of nickel content of olivine versus modal abundance of pentlandite (Fig. 18b) is very similar to that of nickel in pentlandite versus pentlandite abundance. For pentlandite abundances below  $\sim 3$  %, a wide variation in the nickel content of olivine is found, but where pentlandite abundance increases, the amount of nickel in olivine shows a pronounced decrease. Samples from the lower cloud-zone highlight the association between nickel-enriched olivine and nickel-enriched pentlandite (Figs. 17, 19).

Distribution coefficients  $(K_D)$  for Fe-Ni partitioning between sulfide and olivine, uncorrected for activity coefficients, were determined for 7 samples. Nickel and iron content of the sulfide assemblage was estimated using electron-microprobe data and modal abundance. Values were computed as

$$K_D = \left(\frac{\text{NiS}}{\text{FeS}}\right)_{\text{sulfide}} / \left(\frac{\text{NiO}}{\text{FeO}}\right)_{\text{olivine}}$$

with concentrations expressed as mole fractions. Calculated values for various assemblages in the Babbitt deposit (Table 5) range from 2.6 to 39.6. These values are extremely variable, and span virtually the entire range of values computed for other magmatic sulfide deposits (*e.g.*, Naldrett 1979, Fleet & MacRae 1983, Thompson *et al.* 1984). It should be noted that these values represent Fe/Ni partitioning on a thinsection scale. Computed  $K_D$  values show little variability at this scale, but are highly variable at larger



FIG. 17. Trends in the iron and nickel contents of pyrrhotite and nickel content of pentlandite throughout the lower portion of drill hole 136.

scales. The differences in computed  $K_D$  values may be related to local control of sulfide-olivine equilibration under a variety of physical and chemical conditions.

### DISCUSSION

Previous isotopic studies by Ripley & Watowich (1982) and Ripley & Al-Jassar (in press) indicate that much of the sulfur in the Babbitt deposit has been derived from metasedimentary country-rocks through devolatilization reactions. However, the isotopic data for the basal-zone mineralization (*e.g.*, large differences in <sup>34</sup>S between country rock and igneous sulfides) strongly suggest that *in situ* derivation of sulfur was unlikely, and that sulfur must have been added to the melt either prior to or dur-

TABLE 3.	CHEMICAL	COMPOSITIONS	<b>TAKEN</b>	ALONG	A	TRAVERSE	THROUGH	CUBANTIE	AND	THE
		ASSOCIATED	) PHASE	SHOW	τ:	IN FIGURE	12			

Analysis	No. 1	2	3	. 4	5	6	. 7
Fe	41.39	40.80	41.38	41.68	41,25	41.67	41.49
Cu	23.57	23.35	22.56	22.51	23.03	22.76	23.27
S	35.46	35.92	35.85	35,50	35.55	35.42	35.99
Total	100.43	100.08	99.78	99.60	99.83	99.85	100.75
		At	omic Pro	portions			
Fe	0.740	0.731	0.741	0.746	0.739	0.746	0.743
Cu	0.371	0.368	0.355	0.354	0.362	0.358	0.366
s	1.106	1,120	1.118	1.107	1,109	1,105	1,122
Total	2.218	2.219	2.214	2.207	2.210	2.209	2.231
		с	hemical	Formula			
Fe	2.00	2.00	2.03	2,03	2.01	2.03	2.01
Cu	1.00	1.00	0.97	0.97	0.99	0.97	0.99
8	3.00	3.00	3.00	3.00	3.00	3.00	3.00

Compositions, obtained with an electron microprobe, are given in the direction of the traverse, beginning in "cubantiz 2" and proceeding to the left-hand margin of "cubanite 1". Data in columns 1 to 5 pertain to cubanite 2, and those in columns 6 and 7, to cubanite 1. Sample 1758, drill hole 136.

ing emplacement. *In situ* derivation of sulfur for mineralization found above the basal zone remains a possibility, especially if xenolith-rich areas represent previous intrusive floors (*e.g.*, Grant & Molling 1981, Rao & Ripley 1983).

Weiblen & Morey (1976) suggested that addition of volatiles to the South Kawishiwi intrusive body occurred late in the crystallization history. This premise is in part based on the increase in An contents of plagioclase within sulfide-bearing marginal overgrowths, which is attributed to a volatilecontrolled lowering of liquidus temperatures. Our data from the Babbitt deposit suggest that compositions and zoning profiles in plagioclase are extremely variable. Abrupt increases in the An content of plagioclase generally occur only within margins containing sulfide inclusions and hence are localized phenomena (Fig. 9). The presence of overgrowth plagioclase is restricted to areas where trapped liquid was present. For this reason the packing arrangement of plagioclase grains is important in interpreting An zoning. For example, two subparallel plagioclase grains with little or no interstitial liquid may not show either included sulfides or a marginal increase in An content. However, isotopic and thermochemical computations (Ripley & Al-Jassar, in press; Ripley & Andrews 1985) suggest that late and in situ derivation of volatile phases was unlikely in the Babbitt area. The textures and presence of abundant chalcopyrite strongly indicate that sulfide saturation was achieved only after initial crystallization of plagioclase, and that the coexisting liquid was enriched in copper. In order to explain the rather abrupt shifts in An content where sulfide inclusions are found, we suggest that crystallization of plagioclase was promoted, and that of Ca-bearing pyroxene depressed in trapped liquid owing to the



FIG. 18. Plots of weight % nickel in pentlandite (A) and olivine (B) versus pentlandite abundance in the sulfide assemblage. X in (A) denote samples from the transition and lower cloud zones.

TABLE 4. SUMMARY OF OLIVINE (O1) AND ORTHOFYROMENE (Opx) COMPOSITIONAL DATA, BABBITT DEPOSIT, DRILL HOLE 136

Sample Depth (m)	01 <sub>Fo</sub>	OLNIO	Opx <sub>En</sub>	Opx <sub>N10</sub>
352.9	na	0.16	na	0.04
371.2	57.5	0.20	65.7	0.05
380.4	47.9	0.16	58.3	0.04
385.9	49.2	0.13	na	na
386.5			50.7	0.03
415.4			59.0	0.03
421.5			46.2	0.04
432.2			45.9	0.04
436.8	44.1	0.10	57.6	na
438.3			48.2	0.04
441.3	32.2	0.14	42.4	0.07
442.9	50.6	0.13	62.9	na
445.9	50.3	0.13	59.4	na
448.9	51.3	0.07	na	0.02
452.0			44.7	0.07
453.5	45.4	0.18	57.3	0.05
455.0	57.0	0.15	67.4	0.03
458.4			47.5	0.06
462.7	44.1	0.14	56.9	0.05
467.2	46.6	0.09	58.6	0.06
471.8	51.4	na	na	na
474.9	45.5	0.13	58.7	0.04
477.9			57.0	0.05
481.0			50.8	na
485.5	48.6	0.17	57.8	na
488.9	47.4	0.11	na	na
491.6	46.6	na	58.9	na
493.1			36.8	0.08
496.2	23.4	0.04	37.4	0.02
497.7	22.7	0.11	41.0	0.04
500.8			41.3	0.02
532.8	23.4	na	44.1	na
534.3			42.8	0.02
543.4			42.7	0.03
544.0	46.3	0.07	56.1	0.03
545.0	42.7	0.07	52.9	0.03



En enstatite, na not analyzed, - - not present. Fo forsterite. Values for NiO in weight %.

FIG. 19. Olivine and orthopyroxene compositional data from the lower portion of drill hole 136.

continued uptake of  $Fe^{2+}$  by a Cu-Fe sulfide phase. The overall Cu-rich nature of sulfide mineralization has been discussed by Rao & Ripley (1983), Pasteris (1984), and Ripley (in press). Copper contents of sulfide assemblages are variable, but values as high as 15 to 20% are not uncommon. Values of the copper/nickel ratio are normally in the range of 5 to 10. Such characteristics are not atypical for flood-basaltrelated deposits, and have led Naldrett (1981) to suggest that the parent magmas for these deposits have been derived from melting of pristine mantle material containing disseminated copper sulfides. In addition to this mechanism for copper enrichment of the magma, Rao & Ripley (1983) have illustrated possible copper-enrichment trends through a combination of fractional crystallization and magma blending.

Isotopic, petrochemical and mass-balance constraints have led Ripley (in press) to suggest that for basal-zone sulfide mineralization at Babbitt, sulfide saturation must have occurred either prior to or during magma emplacement. A process is envisioned whereby a magma is enriched in copper through mechanisms described by Rao & Ripley (1983), but within an auxiliary chamber located at depth. Calculations utilizing the approach outlined by Campbell & Naldrett (1979) and Campbell & Barnes (1984) show that mass ratios of silicate to sulfide liquid of ~ 1000 to 3000 are required in the auxiliary chamber to explain the Cu and Ni contents of massive mineralization. The occurrence of massive to semimassive mineralization in metasedimentary host rocks at Babbitt suggests that a sulfide-rich liquid was physically capable of infiltrating country-rock material. The cross-cutting nature of the sulfide mineralization and the distinct isotopic difference between massive, Cu-rich ore and disseminated pyrrhotite in country rocks preclude a possible origin through metamorphic segregation of sedimentary material.

Although distinct areas of nearly massive pyrrhotite and cubanite-chalcopyrite locally occur in both igneous and metasedimentary host-rocks, there is no spatial distribution that suggests that massive mineralization resulted from filter pressing of a Cu-rich sulfide liquid away from a crystalline pyrrhotite or monosulfide solid-solution mss (e.g., Craig & Kullerud 1969). However, a plot of copper assays versus % sulfur for samples from the 1700 level (Fig. 20) clearly shows two distinct clusters. One group of samples shows copper values less than 1.1%, whereas the other is characterized by values in excess of 1.5 % copper. Within each group there is a general

DISTRIBUTION OF IRON AND NICKEL BETWEEN SULFIDE AND CLIVINE, DRILL HOLE 136, BABBITT DEPOSIT TABLE 5.

Sample Depth (m)	N1S/FeS	N10/FeO	ĸ
371.2 380.4 445.9 448.9 474.9 488.9 544.0	0.0323 0.0102 0.0077 0.0760 0.0260 0.0143 0.0532	0.00532 0.00340 0.00300 0.00192 0.00266 0.00253 0.00151	6.1 3.0 2.6 39.6 9.8 5.7 35.2



FIG. 20. Plot of copper *versus* sulfur (weight %) from the 1700 level, Babbitt deposit. Two distinct populations of sulfide appear to be present.

tendency for copper content to increase with sulfur content, with copper content of the lower-grade assemblage apparently limited to a maximum value near 1 % copper. These two populations are spatially distinct (Fig. 4), and sulfur isotope values (Ripley & Al-Jassar, in press) also show quite different ranges. Isotopic and chemical data suggest that either a process of fractional crystallization occurred through which a Cu-rich sulfide liquid was separated from silicates and dispersed sulfide (rather than massive mss), or the sulfide assemblages result from distinct mineralizing events. Both the relationship between Cu and S detected in the disseminated mineralization and its characteristic isotopic composition suggest an origin distinct from that of the massive mineralization. In either case, available evidence suggests that sulfide saturation and at least partial accumulation of a sulfide liquid occurred at depth. Basal-zone mineralization at Babbitt was strongly related to the emplacement of a sulfide-rich magmatic liquid whose history was marked by interaction with country rocks as well as by fractional crystallization.

Differences in sulfide mineralogy (particularly cubanite distribution), patterns of distribution, pent-

landite compositions, and olivine-orthopyroxene compositions determined in this study suggest that sulfide generation in the Babbitt area was a complex process, occurring through a range of physical and chemical conditions. Individual sulfide zones and styles of mineralization may be characterized by quite different genetic histories, and several periods of sulfide generation (see, for example, Pasteris 1984, Foose & Weiblen, in press, Ripley, in press) are undoubtedly represented at Babbitt.

Data gathered in this study relevant to the interpretation of sulfide genesis at the Babbitt deposit indicate the following:

1) Cubanite occurs throughout the sulfide-bearing zones at Babbitt, but is the predominant Cu-sulfide where the sulfides exceed  $\sim 6$  vol. %.

2) Within the mineralization of the basal zone, two distinct populations of sulfide are recognized. One is characterized by a copper content less than 1 wt. %, the other by a copper content in excess of 1.5 wt. %.

3) The copper ore-grade tends to be highest in highsulfide zones, but the relative copper content of the sulfide phase increases upward through the disseminated and cloud-zone mineralization. This trend is accompanied by an increase in abundance of chalcopyrite over cubanite.

4) Massive mineralization occurs uncommonly at Babbitt, but is common in the region called the Local Boy deposit, where host rocks include both metasedimentary and igneous units.

5) Disseminated mineralization in the basal sulfide zone and in the overlying cloud-zones is at times difficult to distinguish, but areas of low abundance of sulfides and high content of xenoliths normally occur between the two.

6) Intervals characterized by variations in pyrrhotite and pentlandite compositions are discernible from the lower cloud-zone through basal-zone mineralization. Within these intervals, pentlandite composition varies with pentlandite abundance.

7) Chemical compositions of olivine and orthopyroxene suggest that magma composition varied throughout the same intervals, and that sulfide evolution must be evaluated in terms of the complete magmatic system.

8) Computed coefficients for the distribution of Fe and Ni between olivine and sulfide range from 2.6 to 39.6, with no spatial trends observed.

9) Nickel content of olivine tends to correlate with pentlandite composition and abundance.

Many of the characteristic features of sulfide mineralization at Babbitt may be explained using the mass-balance and element-distribution approach developed by Campbell & Naldrett (1979). Compositional variations between sulfide assemblages may be attributed to equilibration of variable amounts of silicate and sulfide liquid. The distribution and

abundance of cubanite at Babbitt are unlike those reported for most magmatic Ni-Cu sulfide deposits, where chalcopyrite is the predominant copperbearing mineral. Our data suggest that cubanite becomes more abundant where the proportion of sulfide is high. Cubanite-bearing assemblages are richer in Fe than assemblages containing an equivalent mass of chalcopyrite. According to Cabri (1973), cubanite in a magmatic assemblage forms by the decomposition of initially crystallized intermediate solidsolution (iss). This process may include reaction between pyrrhotite and chalcopyrite to produce additional cubanite. We suggest that the principal difference in copper content and mineralogy between disseminated and massive mineralization is related to the amount of sulfide in the system and the metal content of the magma. Compositional data from troctolitic suites of the Duluth Complex (e.g., Weiblen & Morey 1976, Grant & Molling 1981, Rao & Ripley 1983, Tyson & Chang 1984) indicate that the parent melts were strongly fractionated and enriched in iron. Given similar copper contents in magmas, the sulfide assemblages that form at low values of R (mass ratio of silicate to sulfide liquid) and high sulfide content will be characterized by lower grades of copper and higher contents of iron than assemblages that form at higher R values and lower sulfide contents. Therefore, where sulfide proportion is low and high R values inferred, the relative amount of chalcopyrite present should R, high-sulfide environment. According to Rajamani exceed that of an assemblage that formed in a low-& Naldrett (1978), the distribution coefficient for copper between sulfide and basaltic liquids is  $\sim 250$ ,  $\Box$ whereas that for iron, although poorly constrained, is considerably lower. These  $K_D$  values also suggest that higher values of the Fe/Cu ratio in high-sulfide zones relative to disseminated mineralization are consistent with formation of high-sulfide zones at lower R values. The combination of relatively high iron content of Duluth Complex magmas and variable R values (perhaps related to sulfur distribution in country rocks) offers a partial solution to the distribution of cubanite in sulfide-bearing zones. Further fractional crystallization of the sulfide liquid may be responsible for spatially associated assemblages of different grades of copper, such as those found in the vicinity of the 1700 level at Babbitt.

An attempt was made to relate cubanite distribution to variations in intensive parameters such as  $f(S_2)$ . However, pyrrhotite compositions proved to be unreliable for estimates of  $f(S_2)$ , yielding extremely high values. Because pyrrhotite is known to re-equilibrate during cooling, pyrrhotite compositions may not be representative of original  $f(S_2)$ conditions. As a check, a log  $f(O_2)$ -log  $f(S_2)$  diagram was constructed for 1000°C and 2 kbar. The presence of ilmenite, pyrrhotite and graphite in the ore zones at Babbitt serves to restrict possible  $f(O_2)$ and  $f(S_2)$  conditions. A computed  $f(CO_2)$  value of 0.06 (Alawi 1985) was used to estimate a lower  $f(O_2)$  value, with the upper limit of graphite stability defining the uppermost  $f(O_2)$  value. Although small perturbations in  $f(S_2)$  and  $f(O_2)$  cannot be documented, a range of  $f(S_2)$  values between  $10^{-2}$ and  $10^{-3}$  is indicated, at  $f(O_2)$  values between  $10^{-10.5}$ and  $10^{-12.5}$ . These ranges are sufficient to induce



FIG. 21. Histogram showing the relationship between pentlandite abundance in the sulfide assemblage and sulfide proportion in the whole rock.

sulfide saturation in basaltic melts (Buchanan & Nolan 1979), but small fluctuations in  $f(S_2)$  or  $f(O_2)$  cannot be correlated with abundance of cubanite or composition of the sulfide assemblage.

Variations in pentlandite compositions are attributable to two principal causes. High-nickel pentlandite from the lower cloud-zone and transition zone between basal and cloud zones (Fig. 11) is believed to have resulted from crystallization of a sulfide liquid that equilibrated with a magma of relatively high nickel content. This premise is supported by the occurrence of high-nickel olivine in association with pentlandite from this zone. The Mg contents of olivine and orthopyroxene also tend to be higher within this interval, supporting the hypothesis that the magma with which the sulfide equilibrated was less fractionated, and characterized by higher nickel contents than magmas that produced the basal-zone sequence.

Our data also suggest that pentlandite composition varies with pentlandite abundance, with highnickel pentlandite correlated with low abundance of pentlandite in the sulfide phase (Fig. 18a). This trend is observed for both high-nickel pentlandite of the lower cloud-zone and pentlandite from basal-zone mineralization. However, the trend is essentially unrelated to the amount of total sulfide present. Figure 21 illustrates that pentlandite most commonly reaches abundances in excess of 10 volume % in samples containing from 3 to 6 volume % sulfide. The abundance of pentlandite in sulfide assemblages from samples containing less than 3 or greater than 6 volume % sulfide is much lower. Variations in pentlandite abundance in sulfide assemblages is thought to be in part related to the timing of sulfide saturation and to the magnitude of R values. Basal zones of sulfides are thought to have formed from a sulfide liquid that separated at depth within an auxiliary magma-chamber. The coexisting silicate liquid was highly fractionated, Cu-enriched, and somewhat depleted in nickel owing to early crystallization of more Mg-rich olivine. Because of the relatively large amounts of sulfide involved (lower Rvalue), the grade of nickel in the sulfide assemblage produced was correspondingly low. For disseminated mineralization with less than  $\sim$  3 volume % sulfide, sulfide saturation may have been achieved late in the crystallization history, from a melt enriched in copper but depleted in nickel by olivine or orthopyroxene formation.

Samples containing 3 to 6 volume % sulfide may represent a unique set of conditions where pentlandite abundance is higher owing to earlier attainment of sulfide saturation at higher *R* values. Characteristic compositional variations may also be related to local sulfide-olivine equilibration, whose effects may otherwise have been masked by either a low or high proportion of sulfide. In particular, the association between nickel contents of olivine and pentlandite and pentlandite abundance (Fig. 18a,b) is most easily explained by local equilibration between sulfides and olivine. Abundant low-nickel pentlandite is produced where the surface area for iron-nickel exchange is the greatest, normally within areas of high content of olivine. Where the surface area for exchange is reduced, the depletion of nickel from olivine is less important, and a decreased proportion of pentlandite slightly richer in nickel forms in the sulfide assemblage. The highly variable nature of computed Fe-Ni distribution coefficients in the pair sulfide-olivine is consistent with a model of locally variable histories of exchange involving olivine and sulfide.

In summary, the Babbitt Cu–Ni deposit is characterized by a history of multiple injections of magma. Sulfide evolution is an integral part of the dynamic system. At least three sulfide-bearing zones exist at Babbitt, most likely related to distinct intrusive episodes. Many of the compositional features of the sulfide mineralization at Babbitt may be explained by a combination of variable metal-content in the magma and variable R values, fractional crystallization, and local sulfide-olivine equilibration.

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