

Sulfide Inclusions Within the B Chromitite, Stillwater Complex, Montana

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Chapter D

Sulfide Inclusions Within the B Chromitite, Stillwater Complex, Montana

By MICHAEL P. FOOSE and SUZANNE W. NICHOLSON

Sulfide inclusions within the B chromitite of the Stillwater Complex, Montana, provide evidence for complex high-temperature magmatic processes associated with chromite precipitation

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CONTRIBUTIONS ON ORE DEPOSITS IN THE EARLY MAGMATIC ENVIRONMENT

DEPARTMENT OF THE INTERIOR

MANUEL LUJAN, Jr., Secretary

U.S. GEOLOGICAL SURVEY

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Sulfide Inclusions Within the B Chromitite, Stillwater Complex, Montana

By Michael P. Foose and Suzanne W. Nicholson

Abstract

Variations in the abundance of chromite locally define seven layers within the upper part of the B chromitite of the Stillwater Complex, Montana. All chromite-rich layers contain sulfide inclusions, which constitute 0.002 to 0.016 volume percent of the rock. The average diameter of inclusions ranges between 11.9 and 18.5 μm . The sulfide inclusions can be divided into three types depending on whether they occur (1) alone in chromite grains, (2) in chromite grains in association with trapped silicate grains, or (3) within olivine and pyroxene. Pentlandite, chalcopyrite, and pyrrhotite are the dominant sulfide phases, occurring as both single-phase and polyphase inclusions. Electron microprobe analyses show that most pentlandites contain 30 to 38 weight percent nickel and 0.4 to 1.3 weight percent cobalt; most pyrrhotites have atomic metal/sulfur ratios between 0.87 and 0.90. The average bulk composition for all sulfide inclusions, estimated from mineral modes and microprobe mineral analyses, is 38.9 weight percent Fe, 17.1 weight percent Ni, 0.45 weight percent Co, 8.3 weight percent Cu, and 35.2 weight percent S. The estimated average Cu/Ni ratio is 0.83.

In addition to changes in chromite abundance, contacts between some of the layers within the upper part of the B chromitite are also defined by abrupt changes in composition of included pentlandite and pyrrhotite, volume of sulfide, number of sulfide inclusions, and distribution of sulfide inclusions within chromite grains. Within some layers, there are systematic upward changes in Co/Ni ratio in pentlandite, the abundance of sulfide, and the size and number of sulfide inclusions.

The sulfide inclusions were trapped either as an immiscible sulfide melt or as sulfide crystals that separated from the silicate liquids from which the B chromitite crystallized. The average ratio of silicate liquid to sulfide melt (R) was large (minimum range of 6,000 to 50,000), so the initial composition of these sulfides was directly controlled by the composition of the silicate liquid with which they were in equilibrium. Some fractional crystallization of the sulfide melt may have occurred before trapping and thereby contributed to the mineralogical diversity observed among inclusions. However, local variations in partition coefficients and in R were probably more important in creating compositional differences among inclusions. The partitioning of elements between silicate liquid

and sulfide melt probably varied as a result of local variations in $f\text{O}_2$. Variations in both $f\text{O}_2$ and R may have resulted from the precipitation and trapping of sulfides in a zone of turbulent mixing between two compositionally and thermally distinct silicate liquids.

Variations in Co/Ni ratio of pentlandite in inclusions reflect compositional variations in the silicate liquid from which the sulfides originally separated. The Co/Ni variations also coincide with abrupt changes in chromite mode, suggesting that several compositionally distinct liquids were involved in forming the B chromitite.

INTRODUCTION

The Stillwater Complex of south-central Montana is one of the world's better known layered intrusions. Most determinations indicate an age of about 2,700 Ma (De Paolo and Wasserburg, 1979), although an older age of 2,896 Ma has also been suggested (Coffrant and others, 1980). The nearly 6 km of exposed stratigraphic section is commonly divided into three major series (fig. 1; Zientek and others, 1985). The Basal series ranges from 0 to 160 m in thickness and consists of two parts. The lower part is composed mostly of heterogeneous rocks containing varying amounts of bronzite, olivine, plagioclase, and augite. Chromite and pigeonite are also locally present. The upper part of the Basal series is mostly bronzite cumulates (Page, 1979; Zientek, 1983; Zientek and others, 1985). It is overlain by the Ultramafic series, which averages about 1,200 m in thickness and consists predominantly of olivine, olivine and bronzite, and bronzite cumulates. Chromite is also locally present and may form seams as much as several meters thick. The approximately 4,000-m-thick Banded series forms the upper part of the complex, its base being defined by the first appearance of cumulus plagioclase above the Ultramafic series. It consists predominantly of cumulus plagioclase with varying amounts of additional cumulus augite, bronzite, and olivine. Paleozoic sedimentary rocks unconformably overlie the Banded series so that the true thickness of the complex is unknown. Subsequent to consolidation, both Precambrian and Laramide deformations have disrupted the intrusion so that it is now exposed only over a strike length of 44 km.

Sulfides occur in each of the three series. They are most abundant in the Basal series, where large tonnages

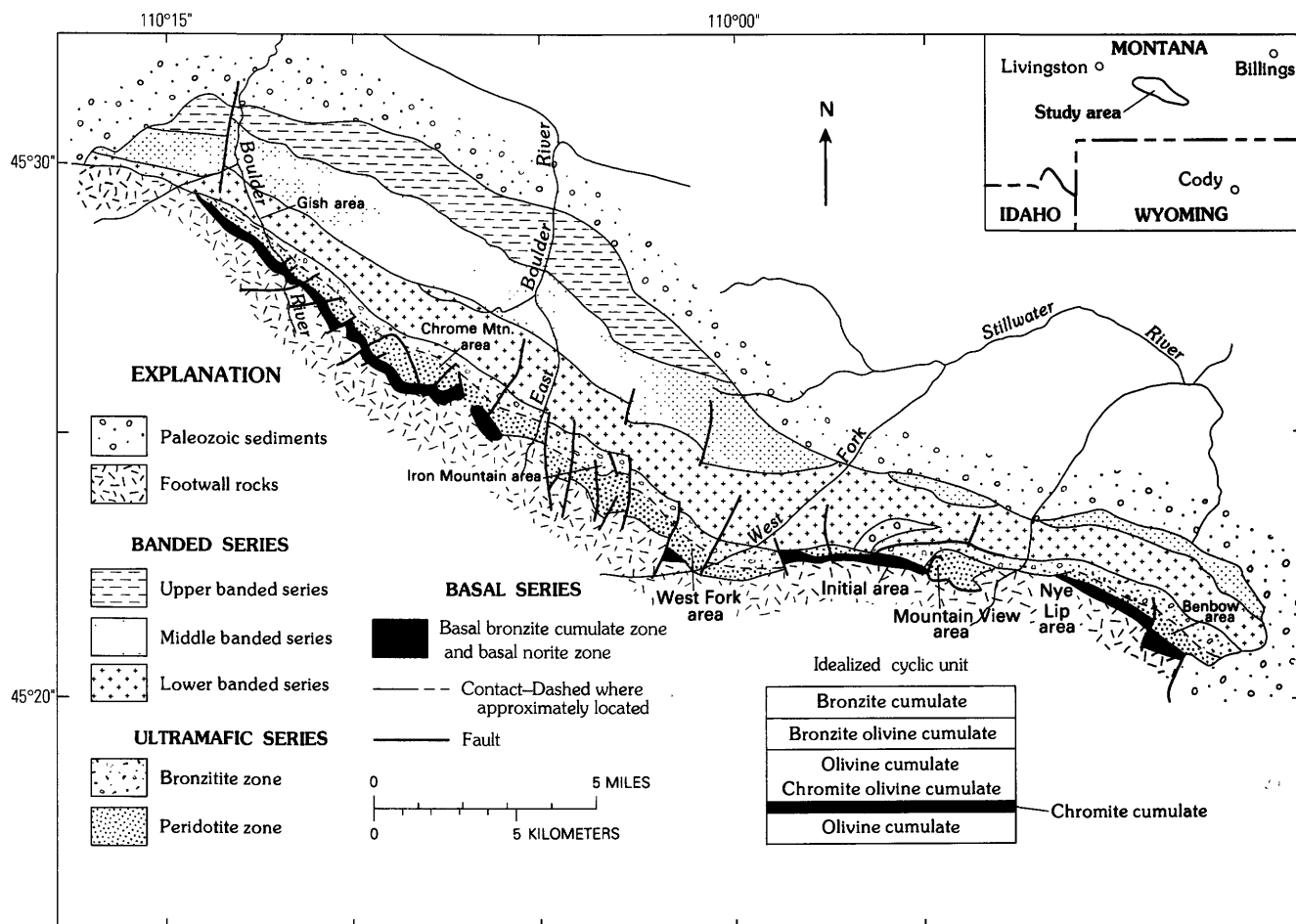


Figure 1. Index and generalized geologic map of the Stillwater Complex, Montana. Map shows distribution of Basal, Ultramafic, and Banded series rocks and location of the West Fork area. Also shown is an idealized chromite-bearing cyclic unit from the Ultramafic series. Modified from Foote (in press).

(>150 million tons) of rock containing about 0.25 weight percent copper and 0.25 weight percent nickel have been identified (Page and others, 1985). Sulfides are rare in the Ultramafic series. Aside from a few small concentrations, sulfides in the Ultramafic series are most conspicuous as inclusions in chromite. The Banded series is known to contain at least 10 sulfide-bearing intervals that range from a few centimeters to several tens of meters in thickness (McCallum and others, 1980; Zientek and others, 1985). The most significant of these is the J-M Reef, a layer that is exceptionally rich in palladium and platinum (locally containing 22.3 grams (0.65 oz) per short ton of palladium and platinum; Todd and others, 1982). It is currently being mined.

Despite their lack of economic significance, the disseminated sulfides in the Ultramafic series are of interest because they provide a link between the copper- and nickel-rich sulfides of the Basal series and the sulfides rich in platinum-group elements (PGE) that occur in the Banded series. The sulfide inclusions within cumulus chromite

grains may also be important as a record of the high-temperature immiscible sulfide melt that was present during the crystallization of the Ultramafic series. Their distribution and composition may, therefore, provide insight into the magmatic processes operating during crystallization of this part of the Stillwater Complex. Sulfides in the B chromite are especially significant because the B chromitite is one of the lowest laterally traceable units in the Ultramafic series.

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This work has benefited from discussions and support from many geologists working both with the U.S. Geological Survey and with the former Anaconda Minerals Company. Particular assistance was provided by B.R. Lipin in collecting the samples used in this work and in providing a detailed stratigraphic description of the B chromitite. N.J. Page shared insights gained from his extensive knowledge of the Stillwater Complex and his similar study of sulfides

in the G and H chromitites. Additional critical comments have been made by G. Czamanske and M. Zientek.

PREVIOUS STUDIES

The geology of the Stillwater Complex has been discussed by Jones and others (1960), Hess (1960), Jackson (1961), Page (1977), and McCallum and others (1980). Most recently, it has been comprehensively reviewed in a special volume (Czamanske and Zientek, 1985). Specific studies of the sulfide minerals in the complex have focused mostly on Basal series rocks (Roby, 1949; Howland, 1933; Page and Simon, 1978; Page, 1979; Humphreys, 1983; Zientek and others, 1982; Zientek, 1983; Drew and others, 1985; Attanasi and Bawiec, 1987) and the recently identified PGE-rich sulfides of the J-M Reef (Conn, 1979; Todd and others, 1979, 1982; Wolfgram and Evans, 1980; Bow and others, 1982; Irvine and others, 1983; Campbell and others, 1983; Barnes and Naldrett, 1985, 1986; Boudreau and others, 1986). Sulfides in the Ultramafic series have been discussed by Page (1972) and Page and others (1985) as part of surveys of sulfide mineral compositions in the Stillwater Complex and were treated in detail in a discussion of sulfide inclusions in the G and H chromitites (Page, 1971).

The B chromitite in the West Fork area was mapped by Howland (1955) who identified it as the "A" chromitite. This designation was maintained in subsequent work by Page and Jackson (1967) on the platinum-group minerals in these chromitites and in studies by Page and others (1969, 1972, 1976) who determined that platinum-group metals in these chromitites show large lateral and vertical variations but on average total 4.6 ppm. B.R. Lipin (*in Mann and others, 1985*) restudied rocks in this area and concluded that these are part of the B chromitite. This identification has been accepted for the purposes of this study.

SETTING OF THE B CHROMITITE

The Ultramafic series, in which the B chromitite occurs, is composed predominantly of cumulus olivine and bronzite. Following the terminology developed by Wager and others (1960) and Jackson (1967), these rocks are olivine cumulates (Oc), olivine-bronzite cumulates (OBc), and bronzite cumulates (Bc). Plagioclase and augite, as well as some olivine and bronzite, fill the intercumulus spaces between grains.

The Ultramafic series is divided into two zones (fig. 1). The upper one-third consists of a sequence of bronzite cumulates that is known as the Bronzite zone, while the lower two-thirds, known as the Peridotite zone, is made up of cyclically layered rocks. Ideally, from bottom to top, cycles consist of layers of Oc, OBc, and Bc that reflect repetitive crystallization of cumulus olivine, olivine +

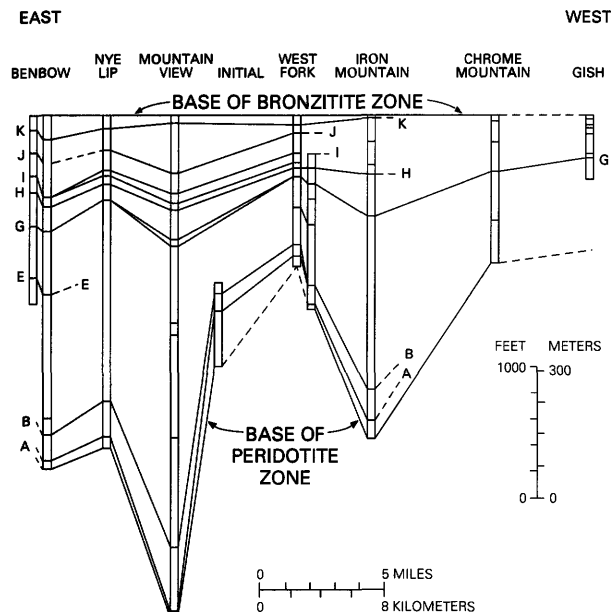


Figure 2. Correlation of chromitites A-K in the Ultramafic series, Stillwater Complex, Montana (from Jackson, 1968).

bronzite, and bronzite. Cyclic units are thought to be caused by influxes of new magma; often magma influxes disrupted this regular crystallization sequence so that these cycles are only partly developed (Jackson, 1970). Between 8 and 21 cyclic units, ranging from 3 to 381 m in thickness, have been identified within the Stillwater Complex (Page, 1977).

Chromite is concentrated as a cumulus phase in the basal parts of some cycles (fig. 1) but commonly does not exceed 2 modal percent. However, the concentration of chromite in several olivine cumulates is sufficient to form laterally continuous layers. In general, these chromitites have sharp basal contacts and grade upward through disseminated chromite into Oc. The most prominent of these chromitites have been labeled according to their stratigraphic position, with A at the bottom and K at the top (fig. 2; Jackson, 1968). Of these, only the G and the H are thick enough to have been mined.

Lipin (*in Mann and others, 1985*) discussed the stratigraphic setting of the B chromitite in the West Fork area (fig. 3). In this area, the B chromitite ranges from about 1.3 to 9 m in thickness. At the specific outcrop examined in this study, it is about 3 m thick, and the upper 1.5 m shows most of the visible internal variation. Twelve samples were collected for study across the upper 1.5 m of this seam. Over this thickness, seven layers can be defined on the basis of abundance of cumulus chromite. From bottom to top, these are:

Layer 1. Net-textured to locally massive chromitite having a sharp upper contact (4 to 6 cm thick).

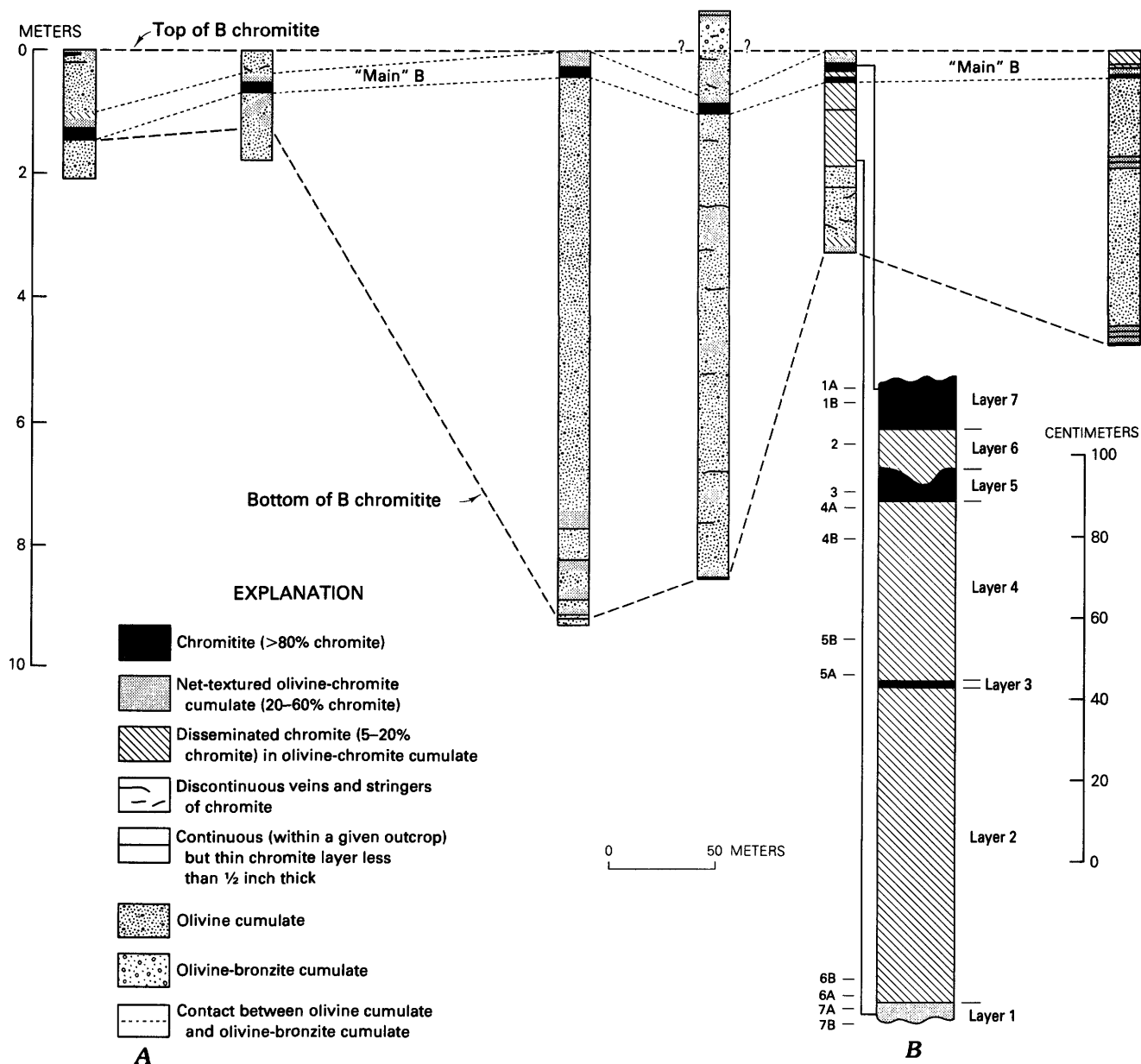


Figure 3. Stratigraphy of the B chromitite in the West Fork area, Stillwater Complex, Montana. A, Local vertical and lateral variations; B, Detailed section and sample locations from the main chromite-bearing portion of the B (modified from Mann and others, 1985). The section studied is located at coordinates 15,320 E. and 21,480 N. on Howland's 1:12,000 map (1955); samples, sample locations, and stratigraphic section provided by B.R. Lipin.

Layer 2. Olivine-chromite cumulate containing 5 to 10 percent chromite (approximately 80 cm thick).

Layer 3. Net-textured to massive chromite (1 to 2 cm thick).

Layer 4. Olivine-chromite cumulate containing 5 to 10 percent chromite (approximately 46 cm thick).

Layer 5. Chromitite with a sharp lower contact and a sharp, but irregular, upper contact (2 to 8 cm thick).

Layer 6. Cross-laminated sequence of olivine-chromite cumulate containing 5 to 10 percent chromite (about 10 to 15 cm thick).

Layer 7. Chromitite, changing from massive at the base to net-textured (12 to 13 cm thick).

METHOD OF STUDY

Polished thin sections from twelve samples collected across the chromite-rich layers were examined in reflected and transmitted light. All sulfide inclusions that appeared to be primary were studied. Inclusions were considered to be primary if they occurred within cumulus grains and were

not associated with fractures. A total thin-section area of approximately 440 cm² was examined, and 1,626 inclusions ranging in size from 1 to more than 100 µm were identified. Each of these inclusions was classified by its setting in enclosing minerals.

Scale drawings of each primary inclusion allowed the size, area, and shape of the inclusions to be catalogued. Drawings were also used to estimate the abundance of each phase within the inclusions and the total volume percentage of sulfide in each specimen.

Electron microprobe analyses were made for pyrrhotite and pentlandite with an ARL EMX SM microprobe using an accelerating voltage of 15 kV and a beam current of 0.1 µA. Synthetic sulfide standards were used, and data were reduced with the ZAF computer program provided by Tracor Northern. Low nickel values were obtained when using this correction package for pentlandite containing 30 to 40 weight percent nickel. Therefore, correction curves determined from analysis of 5 standards containing 9.89 to 73.3 weight percent nickel were used to obtain nickel values for unknowns. Estimated errors based on repeated analyses of standards are 0.3 weight percent for iron and sulfur, 0.2 weight percent for cobalt, and 0.4 weight percent for nickel.

Modal estimates of the abundance of the three major sulfide phases and the microprobe analyses of pentlandite and pyrrhotite were integrated to obtain an estimate of the bulk sulfide composition for each sample. In another study of sulfide inclusions, Czamanske and Moore (1977) obtained this type of information by using a broad microprobe beam and moving it in a stepwise fashion to cover the entire inclusion. This procedure was satisfactory in their study because the sulfide melt was quenched rapidly, causing exsolution in these sulfides to occur as very fine lamellae. In contrast, exsolution in the B chromitite inclusions is relatively coarse, so that averaging the modes from individual inclusions and integrating with sulfide mineral analyses is the most effective way to estimate a melt composition.

OCCURRENCE OF SULFIDES

Sulfide inclusions in the upper part of the B chromitite typically are small and sparsely disseminated. Comparison of the area of sulfide to the total thin-section area indicates that primary sulfides average between 0.007 and 0.008 percent of the rock and range from 0.002 to 0.016 percent (table 1). Diameters of inclusions vary from 1 to more than 100 µm and average between 11.9 and 22.8 µm.

Inclusion Types

Primary sulfide inclusions are divisible into three groups. Type 1 inclusions occur in isolation within chromite grains. Type 2 inclusions are also trapped in chromite but

Table 1. Average size and abundance of sulfide inclusions in the upper part of the B chromitite, Stillwater Complex, Montana

[---marks contact between layers defined by chromite mode]

Sample	Average area (µm ²)	Average diameter (µm)	Volume percent of rock
1A	270	18.5	0.007
1B	233	17.2	.007

2	206	16.2	.003

3	221	16.8	.013

4A	410	22.8	.009
4B	322	20.2	.007
5B	138	13.2	.002
5A	148	13.7	.003

6B	112	11.9	.005
6A	191	15.6	.016

7A	153	13.9	.004
7B	198	15.9	.011

are associated with included silicate. Type 3 inclusions are trapped within primary silicates (generally olivine and pyroxene). Examples of these three inclusion types are shown in figure 4.

Type 1 and 2 inclusions occur in cumulus chromite grains, and type 3 inclusions occur in both cumulus and intercumulus silicate grains. In this part of the B chromitite, cumulus olivine is by far the most abundant primary silicate, and only a few type 3 inclusions are enclosed in intercumulus augite or bronzite. Visual inspection failed to show any discernible difference between inclusions in olivine and those in pyroxenes, and the relatively few inclusions hosted by pyroxene made classifying them as a separate group impractical.

The distribution of inclusions by type (table 2, fig. 5) shows that most occur as inclusions in chromite. To some extent, this association is controlled by chromite mode, but type 1 and 2 inclusions predominate in samples containing only 5 to 10 percent chromite. It is also apparent (fig. 5) that type 1 sulfide inclusions are more common than type 2.

Sulfides may be trapped in adcumulus rims around cumulus chromite grains. Although no practical way exists to unequivocally separate such inclusions, type 1 inclusions were subdivided into those hosted near rims of chromite grains and those occurring near grain centers. This subdivision reveals marked variations between samples. Some contain abundant inclusions near edges of chromite grains, while other samples do not (table 2). A similar subdivision was made for type 2 inclusions, but no difference in distribution was detected.

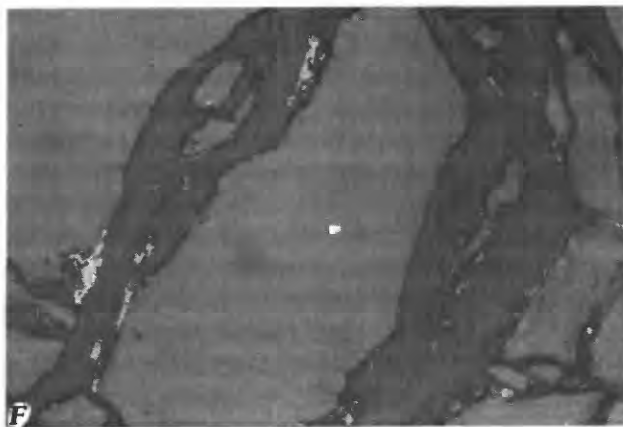
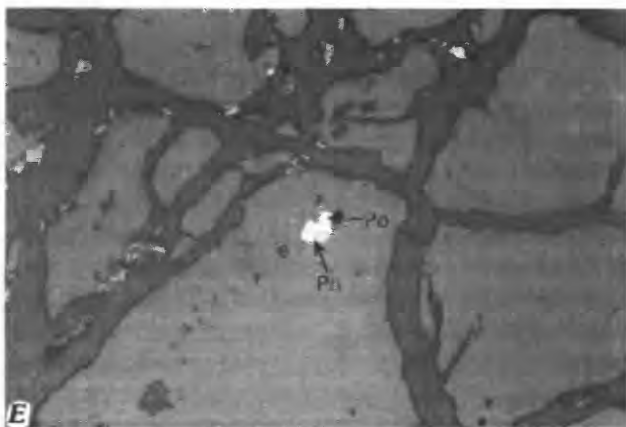
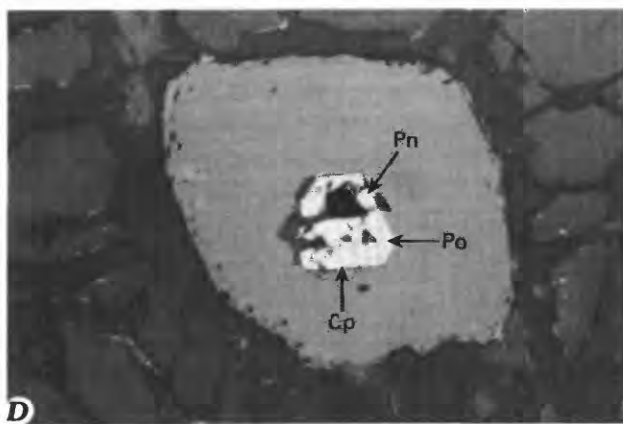
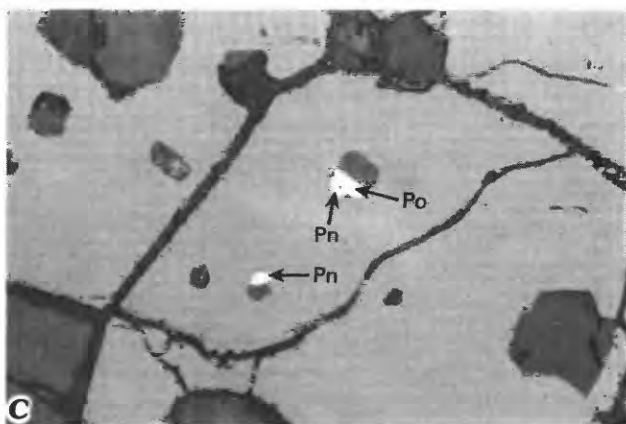
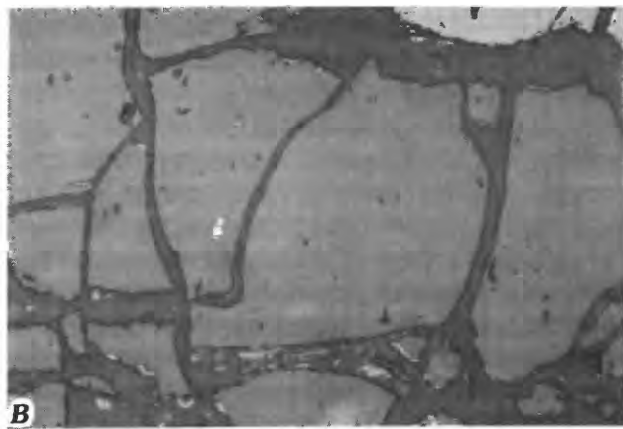
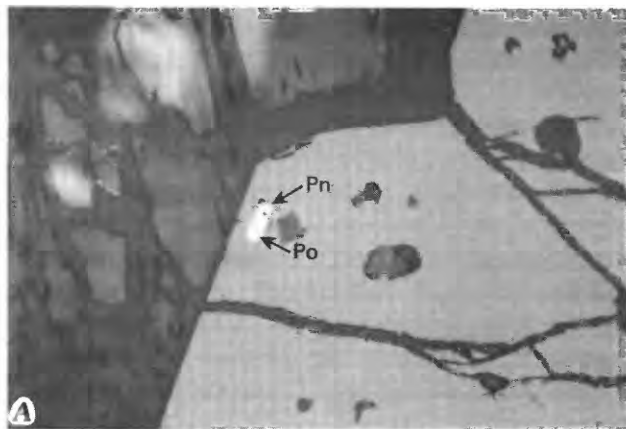


Figure 4. Sulfide inclusion types in the upper part of the B chromitite, Stillwater Complex, Montana. *A*, Type 1 inclusion consisting of pentlandite (Pn) and pyrrhotite (Po) (sample 6A); *B*, Type 1 inclusion containing only pentlandite (sample 7B); *C*, Type 2 inclusions (sample 7B); *D*, Type 2 inclusion containing pentlandite, pyrrho-

tite, and chalcopyrite (Cp) (sample 6A); *E*, Type 3 inclusion containing pyrrhotite and pentlandite in olivine (sample 2); *F*, Type 3 inclusion consisting only of pentlandite in olivine (sample 2). All photographs in reflected light; field of view 0.36 by 0.51 mm.

Included sulfide grains may be euhedral or anhedral. In type 1 and 2 inclusions, sulfides typically have euhedral to subhedral crystal forms where bounded by chromite and are anhedral against included silicates. Grains in type 3 inclusions are mostly anhedral.

Inclusion Mineralogy

Pyrrhotite, pentlandite, and chalcopyrite are found in inclusions. In polished section, sulfide inclusions commonly contain a single sulfide phase (table 3), which, in

Table 2. The distribution by type of sulfide inclusions in the upper part of the B chromitite, Stillwater Complex, Montana [Type 1, occurring within chromite grains without accompanying trapped silicates; type 2, occurring within chromite grains with accompanying trapped silicates; type 3, occurring within silicate grains. ---marks contact between layers defined by chromite modes]

Sample	Type 1			Type 2		Type 3		Total number of inclusions	Modal percentage of chromite in rock
	Cores*	Edges**	Percent	Number	Percent	Number	Percent		
1A	76	1	62.1	47	37.9	0	0.0	124	80
1B	27	22	38.9	76	60.3	1	.8	126	85

2	5	0	9.3	5	9.2	44	81.5	54	5

3	78	84	71.3	65	28.6	0	0	227	90

4A	4	1	6.8	32	43.8	36	49.3	73	5
4B	9	0	11.0	55	67.1	18	21.9	82	5
5B	14	32	68.6	11	16.4	10	14.9	67	5
5A	37	33	72.9	22	22.9	4	4.2	96	10

6B	18	19	25.5	10	6.9	98	67.6	145	5
6A	63	176	76.3	45	14.4	29	9.3	313	70

7A	19	42	55.5	36	32.7	13	11.8	110	10
7B	51	106	75.1	49	23.5	3	1.4	209	45

* Number of inclusions within the cores of chromite grains.

**Number of inclusions near edges of chromite grains.

most cases, is pentlandite. Two-phase assemblages, which are less common, generally consist of pyrrhotite and pentlandite. Inclusions containing all three of the major sulfide phases are relatively rare. Other rare sulfide phases observed in inclusions are heazlewoodite, niccolite, and sperrylite.

Modal proportions of pyrrhotite, chalcopyrite, and pentlandite were determined for all primary inclusions (table 4, fig. 6). Differences between these data and those in table 3 are largely attributable to small inclusions ($<1\ \mu\text{m}$), which strongly influence data on the abundance of inclusions (table 3) but have little effect on the overall modal composition.

Pentlandite is the dominant phase in most samples and is followed in abundance by pyrrhotite and chalcopyrite. In some samples, different inclusion types have approximately similar modal compositions. In other samples, apparent differences in modal mineralogy between inclusion types may be due to the large deviation expected in data obtained from small sample populations. However, data for samples 3, 5B, and 6B appear to be sufficiently abundant to suggest that some real differences in modes exist. These differences do not appear to have any pattern.

Inclusion Chemistry

Microprobe analyses of pyrrhotite and pentlandite were obtained from some sulfide inclusions. The small size of most inclusions, and the polyphase nature of many, made accurate analyses of individual phases difficult to obtain. As a result, the data presented in table 5 are not statistical averages of large numbers of points but instead are considered to be representative of the sample. For pentlandite, the analyses used were those showing the highest nickel contents (indicating the least chance of contamination by pyrrhotite); for pyrrhotite, analyses showing the lowest nickel and cobalt contents were used.

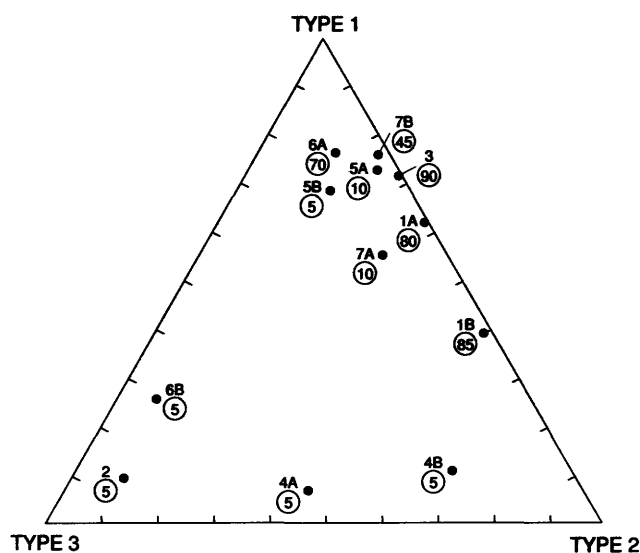


Figure 5. Relative abundance of inclusion types in samples from the B chromitite, Stillwater Complex, Montana. Type 1, sulfides trapped in chromite without accompanying silicates; type 2, sulfides trapped in chromite with silicates; type 3, sulfides occurring within silicate grains. Circled numbers denote modal percentages of chromite in samples.

Table 3. The distribution of mineral assemblages in sulfide inclusions in the upper part of the B chromitite, Stillwater Complex, Montana

[In percent. Po, pyrrhotite; Pn, pentlandite; Cp, chalcopyrite; Ni, niccolite; Sp, sperrylite; Hz, heazlewoodite; ---, none found]

Assemblage	1A	1B	2	3	4A	4B	5B	5A	6B	6A	7A	7B
Po	6.2	5.3	9.2	10.0	13.6	20.8	18.0	3.0	37.1	10.4	14.5	19.6
Pn	26.2	34.7	18.2	20.3	47.3	26.9	10.0	41.8	15.7	24.2	27.0	16.4
Cp	10.8	17.1	20.4	44.7	13.5	12.7	56.0	1.5	14.8	15.4	12.5	8.2
Po+Pn	27.6	24.0	40.9	7.5	20.2	30.2	---	38.8	27.8	38.3	35.8	44.0
Po+Cp	4.6	5.1	4.5	8.8	---	3.1	4.0	4.5	2.8	3.0	6.2	2.3
Pn+Cp	18.5	8.0	6.8	5.6	2.7	1.6	6.0	4.5	.9	3.1	1.0	3.7
Po+Pn+Cp	4.6	5.1	---	2.5	2.7	---	6.0	5.9	---	1.1	1.0	2.2
Ni	---	---	---	---	---	---	---	---	---	---	1.0	2.9
Ni+Pn	---	---	---	---	---	2.0	---	---	.9	---	---	---
Hz	---	---	---	.6	---	---	---	---	---	---	---	---
Po+Hz	1.5	.7	---	---	---	---	---	---	---	.5	1.0	---
Sp	---	---	---	---	---	2.7	---	---	---	3.0	---	.7
Sp+Pn	---	---	---	---	---	---	---	---	---	.5	---	---
Ni+Pn+Po+Hz	---	---	---	---	---	---	---	---	---	.5	---	---

Table 4. Modes of sulfide phases in inclusions in the upper part of the B chromitite, Stillwater Complex, Montana

[Type 1, sulfides trapped in chromite without accompanying silicates; type 2, sulfides trapped in chromite with silicates; type 3, sulfides occurring within silicate grains. Cp, chalcopyrite; Po, pyrrhotite; Pn, pentlandite. Number of points counted; number in parentheses is percentage]

Sample	Type 1			Type 2			Type 3			All		
	Cp	Po	Pn	Cp	Po	Pn	Cp	Po	Pn	Cp	Po	Pn
1A	392 (16.2)	698 (28.9)	1323 (54.8)	3313 (20.6)	5763 (35.8)	7008 (43.6)	0 (0.0)	0 (0.0)	0 (0.0)	3705 (20.0)	6461 (34.9)	8331 (45.1)
1B	1699 (26.5)	1006 (15.7)	3700 (57.8)	2564 (19.3)	1112 (8.4)	9618 (72.3)	0 (0.0)	0 (0.0)	0 (0.0)	4263 (21.6)	2118 (10.7)	13318 (67.7)
2	55 (61.8)	17 (19.1)	17 (19.1)	44 (13.2)	112 (33.6)	177 (35.1)	1007 (16.7)	2429 (40.3)	2587 (42.9)	1106 (17.1)	2558 (39.7)	2781 (43.2)
3	10688 (69.6)	1958 (12.7)	2714 (17.7)	4619 (26.5)	2357 (13.5)	10458 (60.0)	0 (0.0)	0 (0.0)	0 (0.0)	15307 (46.7)	4315 (13.2)	13172 (40.1)
4A	0 (0.0)	133 (37.5)	222 (62.5)	918 (5.6)	1360 (8.4)	13985 (86.0)	920 (22.5)	1041 (25.4)	2130 (52.1)	1838 (8.9)	2534 (12.2)	16337 (78.9)
4B	75 (12.1)	344 (55.4)	202 (32.5)	3371 (23.6)	5677 (39.7)	5262 (36.8)	302 (11.6)	762 (29.4)	1532 (59.0)	3748 (21.4)	6783 (38.7)	6996 (39.9)
5B	1519 (55.1)	841 (30.5)	397 (14.4)	598 (36.7)	858 (52.7)	171 (10.5)	1096 (74.1)	248 (16.8)	135 (9.1)	3213 (54.8)	1947 (33.2)	703 (12.0)
5A	580 (12.7)	1547 (33.8)	2445 (53.5)	505 (14.4)	685 (19.6)	2312 (66.0)	552 (57.9)	99 (10.4)	303 (31.8)	1637 (18.1)	2331 (25.8)	5060 (56.0)
6B	1983 (43.6)	1125 (24.8)	1435 (31.6)	174 (16.3)	120 (11.3)	771 (72.4)	1105 (20.8)	2771 (52.1)	1448 (27.2)	3262 (29.8)	4016 (36.7)	3654 (33.4)
6A	1718 (9.4)	4469 (24.5)	12056 (66.1)	2776 (16.5)	4159 (24.8)	9852 (58.7)	1989 (29.5)	2369 (35.1)	2394 (35.5)	6483 (15.5)	10997 (26.3)	24302 (58.2)
7A	314 (4.3)	2894 (39.7)	4082 (56)	1292 (50.0)	103 (4.0)	1184 (45.9)	21 (1.8)	563 (49.2)	561 (49.0)	1627 (14.8)	3560 (32.3)	5827 (52.9)
7B	2305 (18.1)	3797 (29.8)	6627 (52.1)	2718 (19.2)	4820 (34.0)	6644 (46.8)	0 (0.0)	443 (62.6)	265 (37.4)	5023 (18.2)	9060 (32.8)	13536 (49.0)

Pentlandite compositions range between 30.3 and 37.8 weight percent (23.6 and 29.4 atomic percent) nickel and 0.45 and 1.3 weight percent (0.23 and 1.0 atomic percent) cobalt; Co/Ni ratios fall between 0.0079 and 0.038. Within previously given estimated analytical errors, pentlandites are stoichiometric. Misra and Fleet (1973) determined the compositions of natural and synthetic pent-

landites in a wide variety of sulfide assemblages. The range of compositions determined in this study is nearly identical to the range of 24 to 29.3 atomic percent nickel observed by them for pentlandites occurring with monoclinic pyrrhotite.

Most pyrrhotites contain 53 to 53.5 atomic percent sulfur, which is consistent with their being monoclinic. Pyrrhotites in several samples (7B, 6A, and 4B), however,

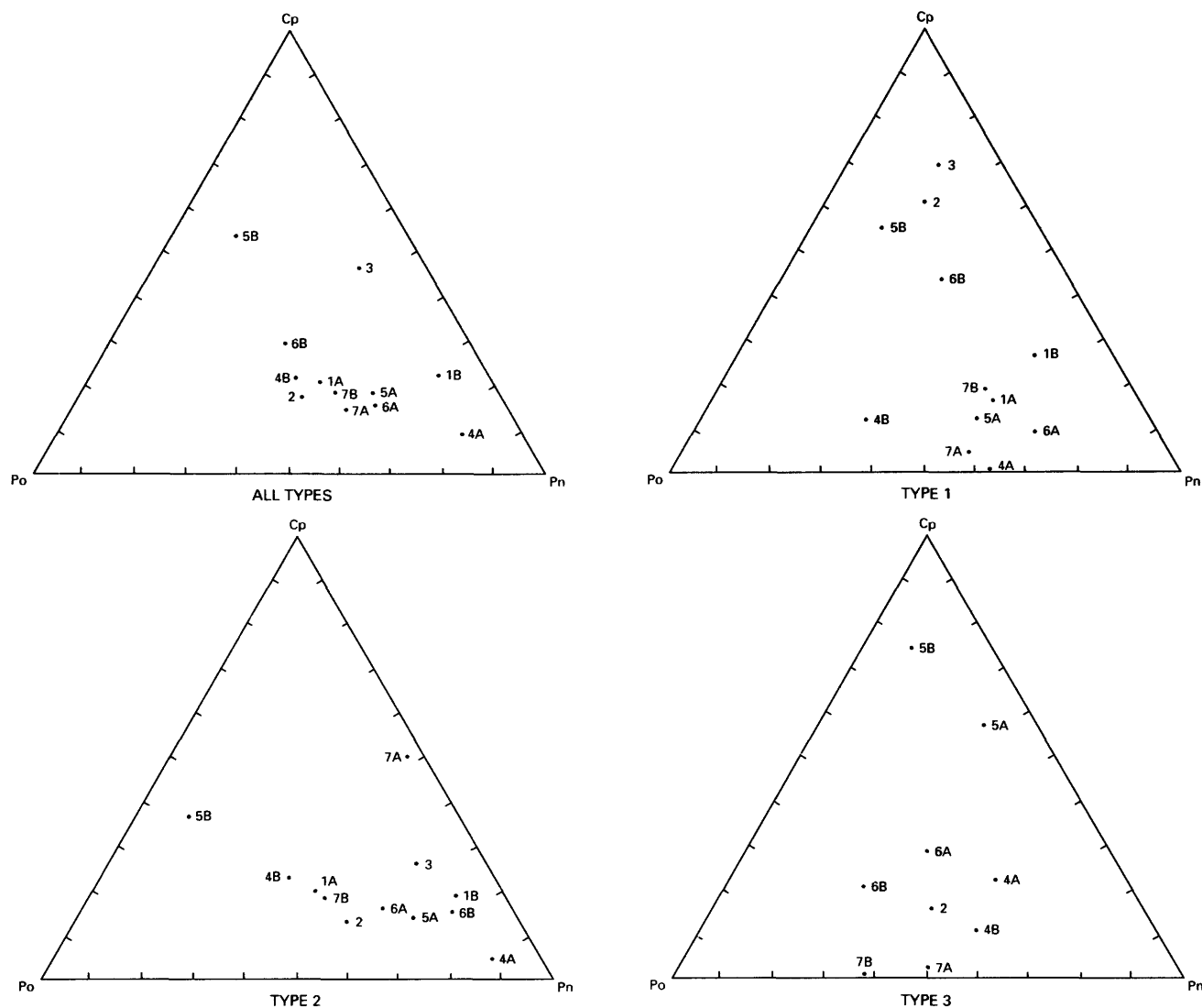


Figure 6. Modes of sulfide phases in inclusions from the B chromitite, Stillwater Complex, Montana. Cp, chalcopyrite; Po, pyrrhotite; Pn, pentlandite. Type 1, sulfides trapped in chromite without accompanying silicates; type 2, sulfides trapped in chromite with silicates; type 3, sulfides occurring within silicate grains.

contain slightly less sulfur, indicating that some hexagonal pyrrhotite must also be present. Nickel and cobalt contents are 0.08 to 0.54 weight percent and 0.02 to 0.41 weight percent, respectively.

Vertical Variations

Compositions of pyrrhotite and pentlandite, volume of sulfide, size of inclusions, proportion of type 1 inclusions, and inclusion mode show vertical variations within the studied section (fig. 7, table 2). Where data are sufficient, variations may be correlated with the variations in chromite mode that were used to define the stratigraphy of this section. From the bottom up, the major characteris-

tics of sulfide inclusions in these seven layers are as follows:

Layers 1 and 2: At the contact between layers 1 and 2, there is an abrupt increase in (1) amount of sulfide, (2) total number of sulfide-bearing inclusions (table 2), (3) percentage of both near-center and near-edge type 1 inclusions, (4) nickel content of pentlandite, and (5) metal/sulfur ratio (M/S) of pyrrhotite. The cobalt content of pentlandite decreases sharply across this contact. There is no discernible change in the relative proportions of the three major sulfide phases.

The limited data from layers 1 and 2 suggest that inclusion size and abundance of type 1 inclusions decrease upward and that abundance of type 2 inclusions increases upward. No data exist for the upper part of layer 2.

Table 5. Compositions of pentlandite (Pn) and pyrrhotite (Po) from the upper part of the B chromitite, Stillwater Complex, Montana

[In weight percent; number in parentheses shows atomic percent]

Sample	Mineral	Fe	Ni	Co	S	Total	Atomic metal/sulfur ratio
1A	Pn	30.5 (24.95)	34.3 (26.69)	0.61 (.47)	33.6 (47.88)	99.01	1.088
	Po	59.7 (46.45)	.37 (0.27)	.03 (.22)	39.3 (53.25)	99.4	.878
1B	Pn	29.1 (23.97)	36.5 (28.60)	.45 (.35)	32.8 (47.07)	98.85	1.125
	Po	59.6 (46.45)	.22 (.16)	.02 (.02)	39.31 (53.37)	99.15	.874
2	Pn	28.5 (23.38)	37.5 (29.26)	.45 (.35)	32.9 (47.01)	99.35	1.127
	Po	59.2 (46.50)	.23 (.17)	.41 (.30)	38.75 (53.01)	98.59	.886
3	Pn	28.27 (23.11)	37.77 (29.37)	.50 (.39)	33.11 (47.14)	99.65	1.121
	Po	60.3 (46.61)	.22 (.16)	.05 (.04)	39.5 (53.18)	100.07	.880
4A	Pn	32.6 (26.61)	33.1 (25.7)	1.15 (.89)	32.9 (46.78)	99.75	1.137
4B	Pn	34.4 (28.18)	30.3 (23.61)	1.06 (.82)	33.2 (47.38)	99.46	1.111
	Po	60.3 (47.43)	.08 (.06)	.05 (.04)	38.3 (52.47)	98.73	.906
5B	Pn	30.6 (25.13)	35.1 (27.41)	.88 (.69)	32.7 (46.77)	99.28	1.138
6A	Pn	28.8 (23.45)	37.6 (29.12)	.99 (.76)	32.9 (46.66)	100.29	1.143
	Po	61.3 (47.83)	.10 (.07)	.05 (.04)	38.3 (52.05)	99.95	.921
7A	Pn	30.7 (25.01)	34.1 (26.43)	1.30 (1.00)	33.5 (47.55)	99.6	1.103
	Po	58.7 (46.27)	.54 (.40)	.06 (.04)	38.8 (53.27)	98.1	.877
7B	Pn	33.0 (26.52)	33.2 (25.38)	1.19 (.91)	33.7 (47.18)	101.09	1.119
	Po	60.1 (47.12)	.52 (.38)	.07 (.05)	38.4 (52.44)	99.09	.906

Layer 3: No data exist for layer 3.

Layer 4: Abundance of type 1 inclusions and nickel content of pentlandite decrease upward, whereas volume of sulfides, inclusion size, abundance of type 2 inclusions, and cobalt content of pentlandite increase.

Layer 5: In comparison to the upper parts of layer 4, there is a marked increase in volume of sulfide, abundance of type 1 inclusions, and modal abundance of chalcopyrite, whereas there is a sharp decrease in inclusion size. Pentlandite composition changes abruptly to be richer in nickel and poorer in cobalt.

Layer 6: Relative to layer 5, volume of sulfide, abundance of chalcopyrite, and proportion of type 1 inclu-

sions decrease. The decrease in the number of type 1 inclusions may be largely attributed to the relative scarcity of chromite in this layer.

Layer 7: Sulfide abundance and inclusion size increase. Pentlandite becomes poorer in nickel and richer in cobalt upward.

In summary, contacts between layers defined by variations in chromite mode are also marked by changes in the character of the sulfide inclusions. The most conspicuous changes are in volume of sulfide, abundance of type 1 inclusions, size of inclusions, and composition of pentlandite. Within layers, type 1 inclusions typically decrease in abundance upward, whereas the proportion of type 2

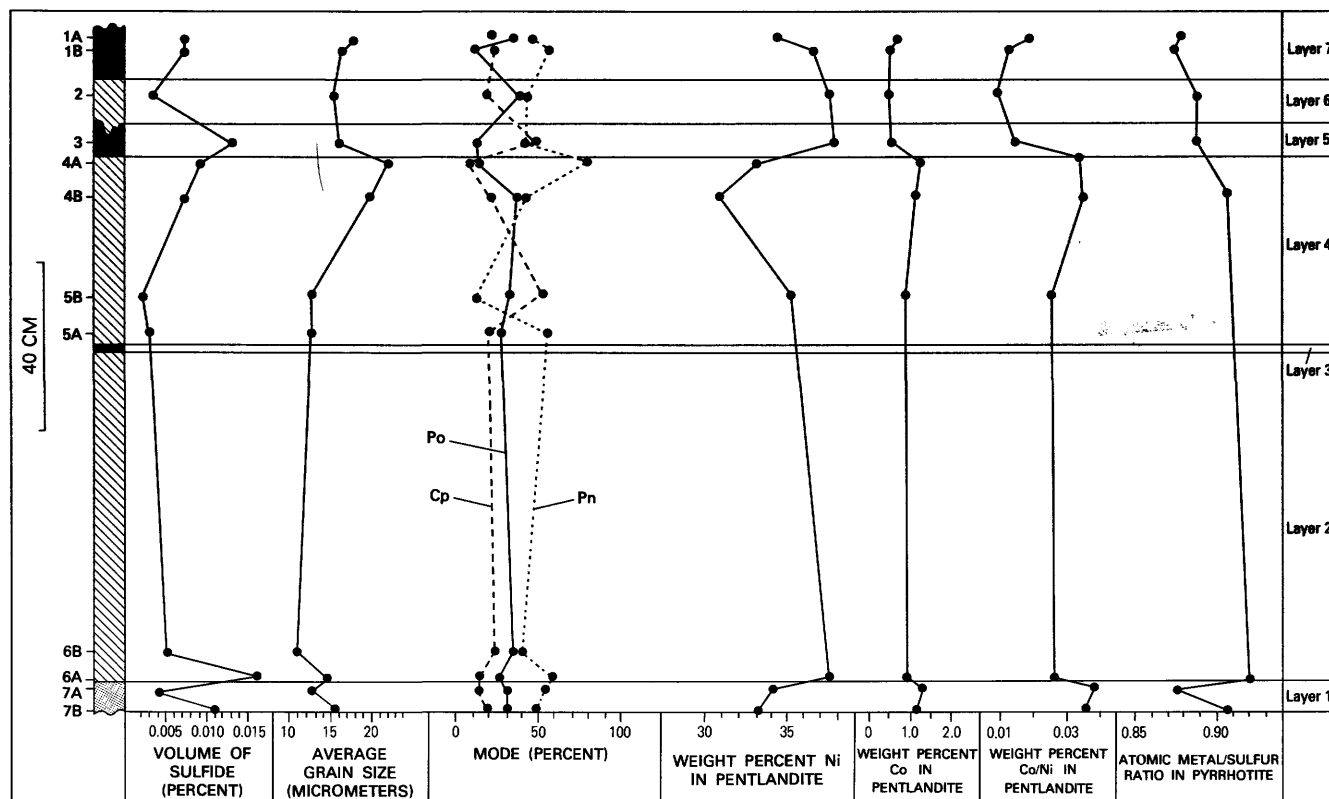


Figure 7. Vertical variations in characteristics of sulfide inclusions in the upper part of the B chromitite, Stillwater Complex, Montana. Horizontal lines separate the seven layers defined by variations in chromite abundance; lithologic symbols are taken from figure 3B.

inclusions increases. Nickel content of pentlandite generally decreases upward. Inclusion size may either decrease or increase.

Bulk Sulfide Composition

Estimates of bulk sulfide composition for each sample were made by integrating the modal data (table 4) with the microprobe analyses of pentlandite and pyrrhotite (table 5). For these calculations, chalcopyrite was assumed to be stoichiometric, and the presence of additional minor phases was ignored. The results are given in table 6 and are plotted along with some experimentally determined phase boundaries in figures 8 and 9. In addition, data obtained by similar methods from the Basal series of the Stillwater Complex are plotted (fig. 8).

The Ni/(Ni+Fe) ratio (weight percent) of the estimated bulk sulfide compositions determined in this study averages 0.30 (range, 0.09 to 0.44). This value is much higher than the values of 0.07 to 0.08 calculated for sulfides in the Basal series of the Stillwater Complex (M.P. Foote, unpub. data). Cu/Ni ratios (weight percent) for bulk sulfide in the B chromitite generally fall between 0.1 and 0.4. Page and Dohrenwend (1973) estimated that the overall Cu/Ni

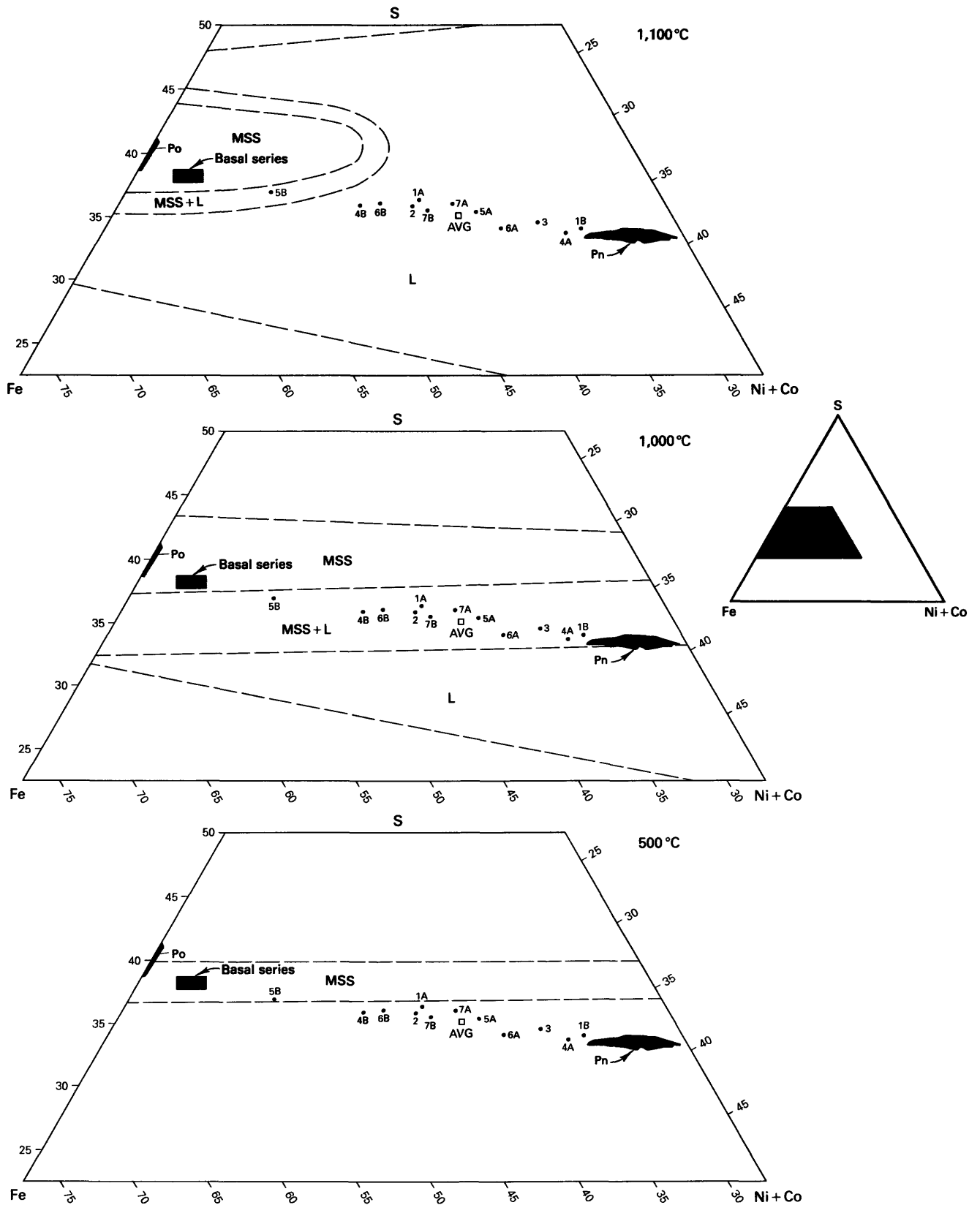
Table 6. Estimated bulk sulfide compositions (weight percent) of inclusions from the upper part of the B chromitite, Stillwater Complex, Montana

Sample	Fe	Ni	Co	Cu	S	Cu/Ni*	Ni/(Ni+Fe)*
1A	41.0	15.8	0.29	6.8	36.1	0.43	0.28
1B	33.0	24.9	.31	7.5	34.3	.30	.43
2	41.5	16.4	.36	5.9	35.9	.36	.28
3	33.6	15.2	.19	16.2	34.9	1.1	.31
4A**	35.1	27.6	.96	2.7	33.7	.10	.44
4B	43.9	12.4	.45	7.4	35.8	.59	.22
5B**	40.3	4.0	.11	19.7	36.0	5.0	.09
5A***	38.6	19.6	.5	6.4	34.8	.32	.34
6B***	41.7	11.8	.3	10.4	35.7	.88	.22
6A	37.5	21.9	.59	5.4	34.6	.24	.37
7A	40.0	18.4	.71	5.1	35.7	.28	.29
7B	41.0	16.8	.62	6.2	35.3	.37	.29
Average	38.9	17.1	.45	8.3	35.2	.83	.30
Standard deviation	3.3	6.0	.23	4.7	.7	1.28	.09

* Weight ratios.

** Calculated by using the pyrrhotite composition of sample 4B.

***Calculated by using the pyrrhotite composition of sample 4B and the pentlandite composition of sample 5B.



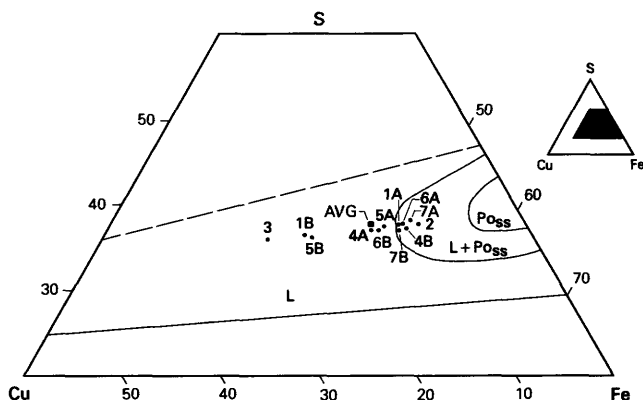


Figure 9. Bulk sulfide compositions of inclusions in the upper part of the B chromitite, Stillwater Complex, Montana, plotted in a portion of the Fe-Cu-S ternary at 1,100 °C. Po_{ss}, pyrrhotite solid solution; L, liquid; AVG, average. Plot is in weight percent and was made after subtraction of amounts of Fe and S needed to make pentlandite. Phase boundaries from Kullerud and others (1969).

ratio for sulfide in the Basal series is about 1.0. However, Zientek (1983) recognized several subdivisions within the Basal series, each having a different Cu/Ni ratio. The Cu/Ni ratios in the B chromitite are slightly higher than the range of 0.02 to 0.25 observed in sulfides at the top of the Basal series and are somewhat lower than both the range found in the lower part of the Basal series (0.4 to 1.5) and the range determined from the dikes and sills below the base of the complex (0.8 to 1.8).

Comparison with the G and H Chromitites

Many of the observations made by Page (1971) on the basis of study of sulfide inclusions in the G and H chromitites are consistent with results from this study. Sulfides in the G and H chromitites have similar abundances (0.007 volume percent in the G and 0.01 volume percent in the H) and similar average diameters (5.5 μm in the G and 11.1 μm in the H). Single-phase inclusions are also common in these two chromitites. The average modal pentlandite/(pentlandite + pyrrhotite) ratio in both the G and H chromitites is 0.68, as compared with the ratio of 0.61 observed in the B chromitite. Finally, estimates based on pentlandite modes suggest that, as in the B chromitite,

◀ **Figure 8.** Bulk sulfide compositions of inclusions in the upper part of the B chromitite, Stillwater Complex, Montana, plotted in the ternary Fe-S-(Ni+Co). MSS, monosulfide solid solution; L, liquid; Pn and Po, fields of observed pentlandite and pyrrhotite compositions, respectively; AVG, average sulfide composition of all inclusions. Plot is in weight percent and was made after subtraction of amounts of Fe and S needed to make chalcopyrite. Phase boundaries from Kullerud and others (1969). Also plotted are some unpublished data from the Basal series.

the Ni/Fe ratio of included sulfides decreases upward in both the G and H chromitites. The B chromitite, however, differs somewhat from the G and H in containing larger, albeit still small, amounts of arsenides. The compatibility of these observations strongly indicates that similar processes were involved in forming the sulfide-bearing inclusions in each of these chromitites.

DISCUSSION

Sulfide inclusions provide clear evidence for the existence of a high-temperature, immiscible sulfide liquid during deposition of this part of the Stillwater Complex. Experimental studies at 1,200 °C show that, under most conditions, silicate liquids containing 10 to 12 weight percent FeO are capable of dissolving about 0.1 weight percent sulfur (Haughton and others, 1974; Buchanan and Nolan, 1979). This range of iron content is characteristic of quench-textured sulfide-free dikes that may represent parental liquids to the Stillwater Complex (Zientek, 1983). An increase in $f\text{O}_2$ or a decrease in $f\text{S}_2$, activity of FeO, or temperature would lower sulfur solubility and cause formation of small amounts of immiscible sulfide melt, as observed in the B chromitite.

Sulfides in a number of mafic magmatic bodies are thought to have been partly derived from sulfur contained in adjacent country rocks. The lack of an identifiable source for external sulfur, the absence of sulfide-rich zones that might result from assimilation of sulfides, and the presence of mantle-type sulfur isotope ratios characteristic of Basal series sulfide-bearing zones (Zientek and others, 1982; Zientek, 1983) make it unlikely that assimilation caused precipitation of the sulfides in the B chromitite.

Accumulation of Sulfides

The accumulation of sulfide melt has been modeled by a process whereby, like falling rain drops, sulfide globules move downward through less dense silicate liquid. Droplets sometimes coalesce to form larger globules that then sink with greater speed (Page, 1979). Sulfide melt may ultimately accumulate at the floor of the magma chamber to form net-textured or massive concentrations. However, calculated settling rates for sulfide inclusions of the size found in the B chromitite are only about 0.25 cm/yr. This calculation is derived from Stokes' Law and is based on an estimated viscosity of 59.1 poise for the silicate liquid, a sulfide density of 4.804 g/cm³, and a silicate liquid density of 2.712 g/cm³ (Page, 1979). On the other hand, Hess (1960) calculated an overall accumulation rate of about 10 cm/yr for the silicates within the entire intrusion, and Jackson (1971) indicated that olivine and chromite in the Ultramafic series would settle at rates greater than 100 m/yr.

These rates indicate that, if sulfides precipitated along with oxides and silicates, most should have been trapped near their point of formation. If, however, significant amounts of sulfide melt had separated before the onset of silicate crystallization, the settling rate of sulfide melt would still have been sufficient to form a thin sulfide layer within 10 to 100 years. Such concentrations are locally observed at bottoms of chromitites (Page, 1971) but are not found in this part of the B chromitite. Finally, although sulfide inclusion size increases downward in some layers, it increases upward in others (for example in layer 4) in a manner not consistent with a settling process. These observations also suggest that the trapping of sulfide inclusions occurred near their point of formation.

Sulfide Inclusion Composition

An unusual aspect of the sulfide inclusions population is the large number of single-phase inclusions (table 3). To some extent, this may result from incomplete exposure of polyphase inclusions in thin section. However, the large number of such inclusions suggests that numerous inclusions consist of only one phase (at least within limits of optical resolution). Page (1971) noted a similar abundance of single-phase inclusions within the G and H chromitites.

When averaged together, data from these B chromitite inclusions yield estimated bulk sulfide compositions that differ from those found in most magmatic sulfide deposits (table 7). Ni/Fe ratios in the inclusions are generally higher than the range of 0.05 to 0.2 typically observed in most deposits, and the range in sulfur content (34 to 37 weight percent) is lower than the 38 to 40 weight percent sulfur typical of most magmatic sulfide deposits (Naldrett, 1981).

However, sulfide inclusions from fresh Mid-Atlantic ridge basalts have bulk compositions similar to those estimated for the B chromitite (Czamanske and Moore, 1977). The average nickel, copper, and sulfur contents in samples from Mid-Atlantic ridge basalts (12 to 15 weight percent Ni, 8 to 10.5 weight percent Cu, and 33.8 to 34.8 weight percent S) overlap the values determined for the B chromitite, while cobalt values from the Mid-Atlantic ridge basalts (average 0.18 weight percent) are somewhat lower. In addition, the abundance (0.022 volume percent) and diameter (5 to 500 μm) of the Mid-Atlantic ridge basalt-hosted inclusions closely match those observed in the B chromitite.

Processes of Inclusion Formation

The compositional diversity shown by individual inclusions in the B chromitite and the unusual bulk sulfide compositions estimated from inclusions within individual samples may be attributed to two quite different processes.

Table 7. Comparison of compositions of sulfide inclusions from the upper part of the B chromitite, Stillwater Complex, Montana, with compositions from diverse magmatic sulfide deposits

[In weight percent. Data from Czamanske and Moore (1977) and Naldrett (1981); ---, no data available]

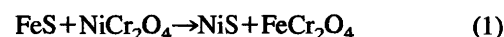
Deposit setting	Nickel	Copper	Cobalt
B chromitite*	11.1–23.1	3.6–13.0	0.22–0.68
Archean komatiite	10–15	0.5–1.5	0.22–0.34
Proterozoic komatiite	10–16	3–4	0.21–0.23
Sudbury	3–6	1–5	0.15–0.20
Flood basalts	4–9	9.7–17	---
Tholeiitic intrusions	4.5–9	1.3–2.5	.2
Mid-Atlantic ridge basalts	12.0–15.5**	8.0–10.5**	0.13–0.25

* Range is plus and minus one standard deviation.

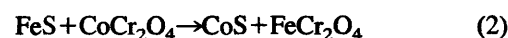
**Range of average values.

First, the compositionally diverse sulfide inclusions may be substantially unchanged since trapping, so that the bulk compositions estimated from them approximate the overall composition of sulfide entrained in the silicate melt. Alternatively, the observed diverse inclusion compositions may result from subsolidus reequilibration between trapped sulfide and the surrounding chromite and silicate.

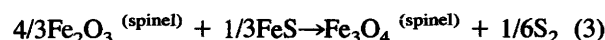
This latter possibility may be illustrated by two types of subsolidus exchange reactions between sulfide inclusions and enclosing chromite grains. The first of these involves exchange of Fe for Ni and Co and involves no loss of sulfur:



and



The second type, suggested by Naldrett and Lehman (1987) and Naldrett and others (1987), involves the diffusion of S through the enclosing chromite:



Fe is used to make additional spinel, and the sulfide is enriched in residual Ni and Co.

All of these reactions would involve small amounts of Fe, Ni, Co, and S. A sulfide inclusion 10 μm in diameter and having the average composition estimated for all inclusions in the B chromitite (table 6) will contain only 1.8×10^{-11} moles of Fe, 6.9×10^{-12} moles of Ni, 2.2×10^{-13} moles of Co, 3.9×10^{-12} moles of Cu, and 2.9×10^{-11} moles of sulfur. If this globule had actually started with a more Fe- and S-rich composition, typical of

most magmatic sulfides (table 7), and changed composition by reactions (1) and (2), the sulfide would have had to lose about 1.1×10^{-12} moles of Fe and acquire about 4.9×10^{-12} moles of Ni and 1.5×10^{-13} moles of Co. If, however, compositional changes occurred as a result of reaction (3), the initial iron-rich sulfide inclusion would have needed to be much larger originally (15 μm in diameter) and would have had to lose about 70 percent of its Fe (6.1×10^{-11} moles) and S (6.5×10^{-11} moles) in order to achieve the average composition observed for the B chromitite sulfide inclusions. The attractive aspect of these reactions is that variations in the amount of subsolidus compositional change may cause inclusions to vary widely in composition, with single-phase inclusions having developed where extensive exchange had occurred.

Several arguments suggest that extensive subsolidus exchange of the types in reactions (1) and (2) has not occurred. The exchange reactions between chromite and sulfide have not been experimentally studied, but those between magnetite and sulfide have. Boctor and Mysen (1980) and Boctor (1981) found that the partition coefficient for nickel between pyrrhotite and magnetite over the range of 600 °C to 300 °C decreased from about 25 to a value between 21 and 15; between 500 °C and 300 °C, the coefficient for Co increased from a value between 2 and 3 to a value between 6 and 10. Thus, with decreasing temperature, sulfide will lose nickel and gain cobalt from magnetite.

The results of these studies are considered to be applicable to reactions involving sulfide and chromite, because the crystal chemistries of magnetite and chromite are similar and because Navrotsky (1975) has shown that the enthalpies of formation of Co- and Ni-bearing magnetite vary over a similar range to the enthalpies of formation of Co- and Ni-bearing chromite.

The partitioning data indicate that any change induced by subsolidus equilibration would have made these inclusions more Fe- and Co-rich. This is inconsistent with the relatively pentlandite-rich mineralogy shown by the entire inclusion population (table 4) and, in particular, by the presence of relatively abundant single-phase inclusions consisting of pentlandite (table 3). Similarly, subsolidus changes should have increased the Co/Ni ratio of the trapped pentlandite. Harris and Nickel (1972), for example, pointed out that pentlandite containing more than about 2 weight percent Co is not typical of magmatic sulfide deposits but has been reported from a variety of nonmagmatic deposits. The compositions determined from pentlandite in individual inclusions (table 5) are not rich in Co.

Similarly, the composition of pyrrhotite in the sulfide inclusions indicates that there has been little uncoupled loss of iron to the surrounding chromite. Such loss of iron would cause a decrease in sulfide metal/sulfur ratio and eventually result in formation of pyrite. Pyrite is not observed in any of the inclusions. Conversely, the addition of iron from

adjacent chromite would cause hexagonal pyrrhotite or ultimately troilite to form. However, most of the pyrrhotites have the lower iron/sulfur ratios of monoclinic pyrrhotite (table 5).

Comparable arguments also suggest that significant changes due to reaction (3) have not occurred. Reaction (3) requires loss of sulfur. If sulfur were not able to diffuse through the chromite structure, the reaction would stop. However, if sulfur were lost, the nickel content of the sulfide would increase until nickel-rich phases like violarite, millerite, and heazlewoodite were stabilized. In many instances, pyrite would be the predicted coexisting iron sulfide. Again, pyrite is not observed, nor is violarite or millerite. Heazlewoodite is present in some inclusions (table 3) but is so rare as to indicate that alteration by reaction (3) has not widely affected all inclusions. Further, compositional change by reaction (3) should necessitate a large volume decrease in the sulfide inclusion, a phenomenon for which no evidence was seen in thin section.

Several additional pieces of evidence argue against substantial subsolidus changes in inclusion composition. First, abrupt changes in the composition of pyrrhotite and pentlandite (fig. 7) are observed to coincide with changes in the B chromitite stratigraphy. These variations also coincide with changes in other characteristics of the inclusions, such as their type, distribution, size, and abundance. If subsolidus changes had altered the composition of inclusions, pyrrhotites and pentlandites within a sample should vary widely in composition as a result of differing amounts of equilibration with their chromite or silicate host. The correspondence of compositional and stratigraphic features evident in figure 7 would not be expected.

Second, the bulk sulfide compositions estimated from these diverse inclusions are similar to the sulfide melt composition in Mid-Atlantic ridge basalts. These bulk compositions are, therefore, present in magmatic systems, even though they are much more nickel rich than compositions reported from most magmatic sulfide deposits.

Third, Lorand (1985, 1987) has documented similar compositionally diverse sulfide inclusions within chromites in upper mantle peridotites. Many of these inclusions, which Lorand showed had escaped chemical alteration, consist of a single phase that usually is pentlandite; the bulk sulfide compositions estimated by using these inclusions are similar to the nickel-rich compositions determined for the B chromitite.

Although it is probable that some subsolidus change in inclusion composition has occurred, the evidence suggests that any such change was local and relatively minor. Thus the overall abundance and composition of these inclusions probably closely reflect the original character of the sulfides before trapping. Therefore, the compositional heterogeneity of inclusions found within single samples must largely result from primary processes.

One process that could result in primary differences in inclusion mineralogy is the fractional crystallization of sulfide liquid. Over the temperature range of 1,100 °C to 1,000 °C in the Ni-Fe-S system (fig. 8), the monosulfide solid solution (MSS) field expands towards the Ni-S join. Most of the estimated bulk sulfide compositions plot in the divariant (liquid + MSS) field present at temperatures between 1,100 °C and 1,000 °C. Therefore, the separation of a nickel-rich liquid from an iron-rich solid would be possible over this temperature range. Upon further cooling to 610 °C, pentlandite would become stable; by 500 °C, exsolution of pyrrhotite and pentlandite from MSS would have been completed in most of these inclusions.

A similar relation exists in the Cu-Fe-S system (fig. 9). At 1,100 °C, many of the estimated sulfide compositions fall in the divariant (pyrrhotite + liquid) field, so that separation of a copper-rich liquid from an iron-rich solid would be possible.

The major problem with this argument is that the temperature at which most of the chromite crystallized appears to have been greater than the temperatures at which fractional crystallization of sulfide is believed to be possible. The temperature of chromite precipitation in the Stillwater is not well known. Jackson (1969) proposed that the G and H chromitites crystallized between 1,300 °C and 1,000 °C on the basis of the compositions of olivine-chromite pairs. This temperature range is probably due to subsolidus equilibration (Irvine, 1967). Estimates based on chromite and olivine compositions from monomineralic layers, where the effects of subsolidus changes would be minimized, indicate temperatures in the middle of Jackson's range (Evans and Frost, 1975). Murck (1985) approached the question differently by analyzing the mechanisms by which Stillwater chromite may have precipitated. She concluded that temperatures of formation were most probably between 1,200 °C and 1,300 °C.

Sharp (1969) and Ryzenkho and Kennedy (1973) showed that the liquidus temperature of pyrrhotite increases about 7 °C/kbar. Therefore, at pressures between 10 and 20 kbar, the sulfide liquidus may approach 1,200 °C. However, pressures of only 3–4 kbar are indicated from contact metamorphosed rocks at the base of the Stillwater Complex (Labotka, 1985). Therefore, the temperature of chromite formation appears to have generally been significantly higher than temperatures at which the processes shown in figures 8 and 9 would have been effective.

Despite trapping temperatures that appear to be too high for significant sulfide fractional crystallization, the fact remains that some type 1 inclusions have shapes of sulfide crystals. This suggests that at least some crystallization of the immiscible sulfide liquid occurred before trapping by some of the chromite. Page (1971) made similar observations on inclusions in the G and H chromitites and was also led to conclude that some crystalline sulfide coexisted with

immiscible sulfide liquid before inclusion in olivine or chromite.

Variations in the ratio of silicate liquid equilibrated with the sulfide melt (R) may provide a second way to explain the compositional diversity among sulfide inclusions. MacLean and Shimazaki (1976) and Rajamani and Naldrett (1978) showed that nickel is much more strongly partitioned into the sulfide phase than is iron. Therefore, the first sulfide to equilibrate with a silicate liquid will be nickel rich. Formation of more sulfide (decreasing R) will rapidly deplete the nickel in the enclosing silicate liquid with the result that the Fe/Ni ratio of subsequent sulfides will increase. Because values of R for the sparsely disseminated sulfides from the B chromitite probably were much greater than those in economic deposits containing vastly larger amounts of sulfides, the Ni/Fe ratio in these inclusions may have been higher than values typically reported for magmatic sulfides.

In most situations, the relation between silicate liquid and sulfide melt can be expressed as (Campbell and Naldrett, 1979)

$$X_{\text{sul}} = X_{\text{sil}} * D_X * (R+1)/(R+D_X) \quad (4)$$

where

X_{sul} is the concentration of trace element X in the sulfide melt;

X_{sil} is the concentration of trace element X in the silicate liquid;

R is the ratio of silicate liquid to sulfide melt; and

D_X is the partition coefficient for trace element X .

This expression shows that, if the composition of the silicate liquid remains constant, the composition of the immiscible sulfide melt will be controlled by R and the partition coefficient D .

The effect on sulfide composition of variations in R and D is shown in figure 10. This plot is made by assuming a silicate liquid containing 350 ppm nickel. This Ni content is consistent with data from dikes at the base of the Stillwater Complex (Zientek, 1983), but this discussion is not critically dependent on it. Nickel partition coefficients are generally considered to range from 275 for basaltic liquids to about 100 for ultramafic liquids (Naldrett, 1981). Estimated values of R in the B chromitite, derived from the volume of sulfide observed in rock, range between 6,000 and 50,000. These are maximum values because individual sulfide inclusions may have equilibrated with smaller volumes of silicate liquid. Over this range of R values and partition coefficients, figure 10 shows that little change in sulfide nickel content can be expected. Czamanske and Moore (1977), however, determined nickel partition coefficients for sulfide globules trapped in Mid-Atlantic ridge basalts that ranged up to 770. With these larger coefficients, variations of up to 5 percent nickel are possible over the

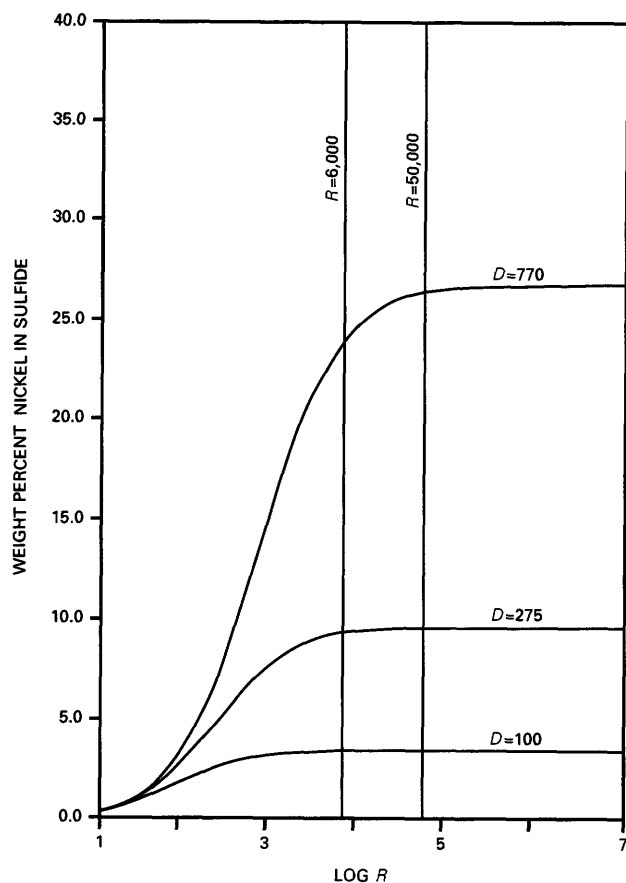


Figure 10. Changes in sulfide nickel content with variations in the ratio of silicate liquid to sulfide melt (R) for different nickel partition coefficients (D). Calculations were made by assuming 350 ppm nickel in the silicate liquid, in agreement with data from Zientek (1983). Values of D are from Naldrett (1981) and Czamanske and Moore (1977).

range in R values given above. Much larger variations in nickel content would be possible if individual inclusions equilibrated with significantly less silicate liquid (smaller R values).

Assuming a partition coefficient of 770 (Czamanske and Moore, 1977), the maximum nickel content in sulfide equilibrated with a silicate liquid containing 350 ppm nickel is about 27 weight percent. This value is close to the maximum nickel content estimated for bulk sulfide trapped in the B chromitite. Since pentlandite in this chromitite averages 34 weight percent nickel (table 5), about 80 percent of a trapped sulfide melt having this bulk composition would ultimately crystallize as pentlandite. The abundance of inclusions apparently consisting of only pentlandite may, therefore, largely result from thin-section exposures that do not intersect the other phases, which make up the remaining 20 percent of the inclusion.

Work by Cowden and Woolrich (1987) and Doyle and Naldrett (1987) indicates that variations in fO_2 will affect the partitioning of metals in sulfide liquids and thus

suggests another mechanism by which primary compositional differences among inclusions might have been generated. Cowden and Woolrich argued that, as fO_2 increases, the number of 6-fold sites in the silicate liquid is reduced. Because Ni^{2+} has a much stronger preference for 6-fold sites than Fe^{2+} , its fractionation into the abundant 6-fold sites present in sulfides is increased. Further, the increase in fO_2 decreases the Fe^{2+}/Fe^{3+} ratio of the silicate melt, making less Fe^{2+} available for partitioning into sulfide. In effect, variations in fO_2 change the nickel partitioning coefficient, such that increases in fO_2 cause marked increases in the Ni content of sulfides. Cowden and Woolrich (1987) concluded that variations in the Fe/Ni ratio in sulfides from Kambalda, Australia, are due to variations in fO_2 and that a change in fO_2 from 10^{-11} to 10^{-10} may cause variations in sulfide nickel content from 9 to more than 20 weight percent. Similarly, in a review of available experimental data, Doyle and Naldrett (1987) demonstrated that variations in the ratio of O/(S+O) may markedly change the exchange coefficient of nickel between sulfide melt and olivine.

Once trapped, sulfides containing different amounts of oxygen may undergo further compositional changes. During fractional crystallization, sulfides that are oxygen rich may crystallize oxides, whereas those that are oxygen poor may form only monosulfide solid solution (Naldrett, 1969). Although magnetite is the most typical oxide to form during crystallization of a sulfide melt, in Cr-rich systems, such as the B chromitite, a Cr-rich spinel may initially form (Czamanske and others, 1976; Ewers and others, 1976; Groves and others, 1977). The chromium in the sulfide melt is quickly depleted so that magnetite is precipitated as rims on the chromite. Therefore, fractional crystallization of sulfide inclusions that initially contained different amounts of oxygen may result in the formation of different amounts of oxides. These oxides most probably would nucleate on the walls of the trapping phase and, because of their small volume, not be observable in these inclusions. Their crystallization, however, could dramatically influence the amount of iron available for incorporation into sulfide and thus control the Fe/Ni ratio in sulfide inclusions.

The local variations in fO_2 required by this mechanism could occur in at least two ways. Ulmer (1969) showed that increases in fO_2 will encourage chromite precipitation and, conversely, that chromite precipitation will tend to lower fO_2 in the silicate liquid. Very local and relatively short-lived variations in fO_2 may therefore be expected in the liquid immediately adjacent to a nucleating and growing chromite grain. Because trapping of the sulfide inclusions is intimately associated with chromite growth, it is possible that, just before trapping, these inclusions equilibrated with silicate liquids having different values of fO_2 .

Alternatively, Murck (1985) proposed that some of the Stillwater chromitites formed as a result of mixing of

magmas that differed both in composition and in temperature. These differences would also virtually insure a difference in fO_2 . For example, two liquids that were both equilibrated with the quartz-fayalite-magnetite buffer but that differed in temperature by 100 °C could easily have differences in fO_2 in excess of 1 log unit. Murck (1985) suggested that temperature differences of 50 °C to 200 °C may exist between the liquids that mixed to form some Stillwater chromites. Calculations by Huppert and Sparks (1980) indicate that mixing of such liquids would be extremely turbulent. The result would be a zone of mixing in which chromite precipitated and in which there were significant local variations both in liquid composition and in fO_2 .

Variation in $Fe^{3+}/(Cr+Al+Fe^{3+})$ has been shown to be a sensitive indicator of changes in magma fO_2 (Ulmer, 1969). Data from the G and H chromitites (Murck, 1985) show local variations in this ratio. In massive chromitites, where effects of subsolidus change should be minimized, this ratio fluctuates between 500 and 800. Hill and Roeder (1974) indicated that this range of compositional variation could occur in basaltic liquids at 1,000 °C by changing fO_2 about one-half log unit.

To summarize, a turbulent-liquid mixing model for formation of the B chromitite allows rapid and localized variation of two important parameters that may cause inclusions to become compositionally diverse. First, large variations in R values could result from turbulent mixing in which individual sulfide globules were trapped before they had completely equilibrated with the surrounding silicate liquid. Second, local variations in fO_2 would occur within the zone of mixing, causing variations in the partitioning coefficients and, perhaps, in the amount of oxide crystallized from the trapped sulfide melt.

Several additional points should be made concerning the effect of these processes on sulfide inclusions. First, although large local variations in inclusion composition may occur as a result of liquid mixing, the entire population of sulfide inclusions within a sample may define an average bulk sulfide composition that reflects the average composition and fO_2 of the silicate liquid forming that part of the B chromitite from which the sample was taken. Second, although changes in fO_2 may dramatically alter the partitioning of nickel into sulfides relative to iron, similar relative changes between nickel and cobalt are not to be expected. Nickel and cobalt have similar octahedral site preferences (Burns, 1970), and, therefore, changes in the structure of the silicate melt as a result of changes in fO_2 should affect the partitioning of nickel and cobalt in similar ways. Therefore, the Co/Ni ratio of the immiscible sulfide liquid should be relatively insensitive to changes in fO_2 and should be controlled principally by the composition of the silicate liquid. Third, any post-trapping crystallization of oxides would alter the amount of Fe in the sulfide but would not affect the proportions of Ni and Co. Fourth, any

subsolidus change in composition as a result of reaction (3) would only involve loss of Fe and S and also would not affect the abundance of Ni relative to Co. Thus, variations in Co/Ni ratio within sulfide inclusions may directly reflect differences in Co/Ni ratio of the silicate liquids from which the sulfides initially separated.

Vertical Changes in Composition

Pentlandite is the only sulfide phase in these inclusions that contains significant amounts of cobalt and nickel. Because cobalt and nickel both prefer the sulfide melt relative to the silicate liquid, variations in the Co/Ni ratio in pentlandite should act as an extremely sensitive indicator of variations in the composition of the silicate liquid. Duke and Naldrett (1978) indicated that the compositions of olivine that separates from a liquid from which 50 molecular percent of the olivine has separated and which has changed its MgO content from about 30 to about 17 percent will range only from $Fe_{94.8}$ to Fe_{89} , whereas the nickel content of sulfides forming over the same crystallization interval will change from more than 17 to less than 2 weight percent.

The pentlandite data (table 5, fig. 7) suggest that at least three compositionally different batches of liquid were involved in the crystallization of the upper part of the B chromitite. The changes in Co/Ni that define these batches occur between layers 1 and 2 and layers 4 and 5. No data are available to determine whether similar changes in liquid compositions occurred in layer 3. Relatively uniform pentlandite compositions in layers 5, 6, and the lower part of 7 suggest that the liquids from which these layers crystallized did not have different Co/Ni ratios.

The sharp shift to lower Co/Ni between layers 1 and 2 and between 4 and 5 is consistent with the introduction of a pulse of more primitive liquid. Where sufficient data exist to make the determination (layers 1, 4, and 7), the Co/Ni ratio increases upward, following the expected pattern for fractional depletion of nickel and cobalt from a silicate liquid.

The two distinct breaks in pentlandite composition are also accompanied by changes in the manner in which sulfides occur. The most noticeable of these changes is an increase, at the base of each section, in the volume percentage of sulfide and in the abundance of type 1 sulfide inclusions. For reasons outlined earlier, this increase in volume percentage of sulfides is not thought to result from gravity concentration of sulfides. Instead, it may reflect the initial reduction in the solubility of sulfur, which may result from mixing two different liquids or from cooling a newly injected liquid against the underlying cumulus pile. Local sulfide supersaturation may also have induced sulfide separation at a large number of sites in the silicate liquid, thus producing the large number of type 1 inclusions found at the bottom of these sections.

CONCLUSIONS

Sulfide inclusions constituting between 0.002 and 0.016 volume percent of the rock and ranging in diameter from 11.9 to 18.5 μm are present within the B chromitite. The inclusions are compositionally diverse. Inclusions having three or more phases are rare; most contain only one or two phases. The estimated average bulk sulfide composition for the inclusions is 38.9 percent Fe, 17.1 percent Ni, 0.45 percent Co, 8.3 percent Cu, and 35.2 percent S. The Ni/(Ni+Fe) ratio of about 0.3 is unusually high and the sulfur content is low when compared to values reported from most magmatic sulfides. These compositions, however, are similar to those of sulfide globules trapped in Mid-Atlantic ridge basalts.

Several arguments suggest that these compositions have not been substantially affected by subsolidus exchange with the surrounding hosts. First, data on sulfide exchange with magnetite suggest that subsolidus equilibration should have decreased the Ni/Fe ratio, a change not supported by the abundance of pentlandite in inclusions. Second, the exchange data indicate that the Co/Ni ratio in these inclusions should increase as a result of diffusion, whereas pentlandites in these inclusions have Co/Ni ratios typical of magmatic deposits. Third, the subtraction or addition of Fe from adjacent chromite should have formed either pyrite or abundant hexagonal pyrrhotite, neither of which is observed. Fourth, diffusive loss of sulfur and iron would ultimately produce nickel-rich phases that are generally not observed. Fifth, changes in inclusion composition occur where there are abrupt changes in the internal stratigraphy of the B chromitite. These changes also coincide with changes in abundance of inclusions, volume of sulfides, and proportion of inclusion types. Post-trapping, diffusion-induced changes should develop locally within the enclosing host mineral so that the observed compositional changes should not correlate with the B chromitite stratigraphy.

Several processes may account for the diversity among individual inclusions and their unusual bulk compositions. Some fractional crystallization of the sulfide melt may have occurred, as indicated by the presence of inclusions having shapes of sulfide crystals. However, this process probably was not important because it would have occurred at temperatures lower than those at which most inclusions were probably trapped. Variations in D (partition coefficients) and R (the ratio of silicate liquid to sulfide melt) are more likely to have affected the inclusion composition. Extremely local variations in D may have resulted from variations in $f\text{O}_2$ as a result of chromite precipitation and (or) mixing of compositionally and thermally different liquids. Sulfide melt trapped under differing $f\text{O}_2$ would have had different Fe/Ni ratios and, after entrapment, may have crystallized different amounts of oxides, thus further altering Fe/Ni ratios of inclusions. Variations in R would result from entrapment of sulfide melt before complete equilibration with the silicate liquid occurred, a process

facilitated by chromite precipitation and sulfide entrapment in a zone of turbulent mixing of two different liquids.

The Co/Ni value of the sulfide melt is relatively insensitive to changes in magma $f\text{O}_2$ and also is not substantially changed by post-trapping precipitation of oxides or loss of iron and sulfur. Variations in this ratio may therefore effectively reflect the composition of the silicate liquid from which the sulfide melt separated. Changes in Co/Ni content of pentlandites occur where there are abrupt changes in the stratigraphy of the B chromitite and indicate that at least three separate pulses of silicate liquid were involved in the deposition of the upper part of the B chromitite. These results support the hypothesis that chromite in the upper part of the B chromitite formed as a result of the mixing of compositionally different liquids.

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