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CHEMICAL COMPOSITION OF ALTERED CHROMITES FROM THE STILLWATER COMPLEX, MONTANA[1]

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ABSTRACT

Small amounts of very iron-rich chromite are formed as an alteration product of normal cumulus chromite accompanying the alteration of primary silicates to chlorite in the Stillwater Complex, Montana. We have analyzed two parent chromite-ferritchromit pairs from the Stillwater Complex by a combination of wet and microprobe methods; both the parent chromite and ferritchromit can be expressed by the general formula (Mg, Fe^{2+}) (Cr, Al, $Fe^{3+})_2O_4$, and neither contains cation deficiencies of the maghemite type. The alteration is essentially a volume-for-volume replacement of MgO and Al_2O_3 by FeO and Fe_2O_3; content is only slightly different in the primary and secondary phases.

INTRODUCTION

Opaque, highly reflecting borders on chromite grains have been described from many Alpine-type ultramafic bodies, but to the authors' knowledge, none has been described from stratiform-type bodies. Most investigators have suggested that these borders are enriched in iron and depleted in Mg and Al (Dresser, 1913; Phillips, 1927; Petrulian, 1935; Horninger, 1941; Spangenberg, 1943; de Wijkerslooth, 1943; Vaasjoki and Heikkinen, 1961; Miller, 1953; den Tex, 1955; Ramdohr, 1960; Panagos and Otteman, 1966; Weiser, 1967; Golding and Bayliss, 1968), but, in general, it has not been possible to determine the distribution of ferrous and ferric iron or to obtain all the information necessary to calculate mass balances.

Considerable variation in the composition of the altered borders is, however, reported by these authors, leading one to conclude that chemical variability of the "ferritchromits[2]" is at least as great as that of the chromites from which they arise. In a study of chromites from 35 deposits, Weiser (1966) concluded that the alteration products could be divided into two groups, the first showing an increase of Fe and Cr and a decrease of Mg and Al, and the second showing an increase of Fe and a decrease of Cr, Al and Mg. He also observed that normally only one of these groups is observed in a single deposit.

The iron-rich chromites of the Bushveld Complex (Kupferbuger and

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[1] Publication authorized by the Director, U. S. Geological Survey.

[2] Spangenberg (1943, p. 23) coined the term "ferritchromit" to refer to an "opaque substance, [that] according to chemical and physical properties, must lie between chromite and magnetite."

Lombaard, 1937; Frankel, 1941; Frankel and Granger, 1941), which are rich in titanium and associated with ilmenite but not chlorite, appear to be entirely different from those described here.

Of more than 100 polished sections examined from the chromitite zones of the Stillwater Complex, ten contain ferritchromit along crystal borders and fractures in the chromite, generally in very minor amounts. Of these, two, both from layers above the G-chromitite zone, contained more than 10 percent. The results from the investigations of these two samples, 53EB-11 and 55WF-3 presented here, have a direct bearing on the argument of constant volume versus constant composition during serpentinization.

Geologic Setting

Nearly all of the chromite in the Stillwater Complex occurs in the Peridotite member of the Ultramafic zone (Jackson, 1961, 1963). The Peridotite member has been divided into 15 subunits called cyclic units. Thirteen of these cyclic units contain recognizable layered concentrations of chromite, called zones. These zones are compound, being usually composed of chromite cumulate layers at the base, giving way upward to alternating olivine-chromite cumulate and chromite cumulate layers. Sample 55WF-3 is from the H-chromitite zone in the West Fork area, and sample 53EB-11 is from a chromitite zone (probably but not surely the H) that lies above the G chromitite zone in the Chrome Mountain area (Fig. 1). Both samples were cut from the basal part of their respective zones (Jackson *et al.*, 1960). Sample 53EB-11 was taken from the foot-wall of a chromitite (chromite cumulate) layer about 6 inches in thickness that is sandwiched between two much thicker layers of serpentinized dunite (originally olivine cumulate). Sample 55WF-3 was collected from a chromitite (chromite cumulate) layer about 2 inches in thickness, underlain by a thick serpentinized dunite (originally olivine cumulate) and overlain successively by a serpentinized section consisting of an olivine chromitite (olivine-chromite cumulate) layer about 6 inches thick that contains 10–15 percent chromite.

As in most areas of local alteration in the Stillwater Complex, the common secondary silicate in the West Fork and Chrome Mountain areas is serpentine. However, the silicate immediately surrounding the ferritchromit in the chromitite zones is chlorite, suggesting that the formation of chlorite is genetically related to the alteration of the chromite. The chlorite in 53EB-11 immediately gives way to serpentine (lizardite) downward in the section as one passes from chromitite into dunite. X-ray diffraction analysis of this serpentine failed to reveal brucite.

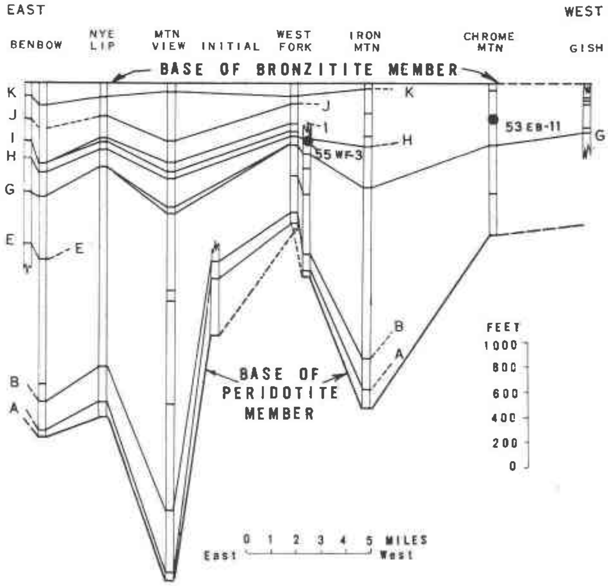

FIG. 1. Correlation of chromitite zones in the peridotite member, Stillwater Complex, (after Jackson, 1963).

PETROGRAPHY

Modal proportions of minerals in samples 53EB-11 and 55WF-3 were determined by point-count methods in both transmitted and reflected light (Table 1). Both samples are normal cumulates in which chromite is the only cumulus mineral. Chromite originally made up 77 volume percent of both 53EB-11 and 55WF-3. Slight postcumulus overgrowth of chromite in 53EB-11 has destroyed some of the euhedral outline of individual crystals. However, there seems to be no special relationship between these overgrowths, which have essentially the same composition as the settled chromite, and the ferritchromit. The chromite crystals contain numerous primary olivine inclusions of Jackson's (1961; 1966) type 2, still fresh where the chromite is unfractured, but chloritized where cut by fractures. The ferritchromit rims, in addition, contain much smaller ragged inclusions of chlorite unrelated to the type 2 inclusions, and these are believed to have formed during the alteration.

The ferritchromit in 53EB-11 shows up in transmitted light (Fig. 2-A) as opaque areas invading the chromite along crystal boundaries and fractures, but must be distinguished from magnetite, which is also opaque but which forms lacy accretions on the margins of the chromite grains.

TABLE 1. MODAL PROPORTIONS OF MINERALS IN TWO SAMPLES OF ALTERED CHROMITITES

Mineral	53EB-11 (Vol %)	55WF-3 (Vol %)
chromite	64.5	64.5
ferritchromit	12.5	12.5
magnetite	2.5	1.0
olivine	0.3	none
biotite	0.7	none
chlorite	19.5	19.9
dolomite	none	2.1
	100.0	100.0

The two are more readily distinguished in reflected light (Fig. 2-B); the reflectivity of ferritchromit is intermediate between that of magnetite and the parent chromite, and the textural relations are generally more clearly displayed. Ferritchromit makes up 12.5–15 percent and magnetite 2.5–3 percent of the rock. As can be seen (Fig. 2 A-B) no zoning is apparent in either the ferritchromit or parent chromite, and the contact between the two phases is very sharp. Some chromite grains are slightly serrate where in contact with the colorless chlorite, but no appreciable replacement of chromite by chlorite was noted. Preservation of the regular crystal outline of the primary chromite grains in altered areas suggests that the alteration is essentially a volume-for-volume replacement.

Postcumulus overgrowth is present to about the same extent in sample 55WF-3 as in 53EB-11, but the rock is more extensively fractured, the fragments being separated or offset. In this sample the rather abundant silicate inclusions are commonly chloritized, presumably because of the abundance of fractures. In contrast to 53EB-11, the ferritchromit and chromite of 55WF-3 have zoned contacts that show up in both transmitted and reflected light as a gradual color value change in the chromite as a ferritchromit boundary is approached (Fig. 3 A-B). The reflectivity of ferritchromit in this sample is closer to that of the parent chromite than in 53EB-11, and the two phases are therefore not so easily distinguished. Again, retention of smooth euhedral grain shapes suggests volume-for-volume replacement of chromite by ferritchromit.

X-RAY DIFFRACTION

Diffractograms of the unseparated chromite-ferritchromit concentrates for 53EB-11 revealed two distinct spinel phases, the dominant one, chromite, having $a = 8.287 \pm .002$ and the subordinant one, ferritchromit,

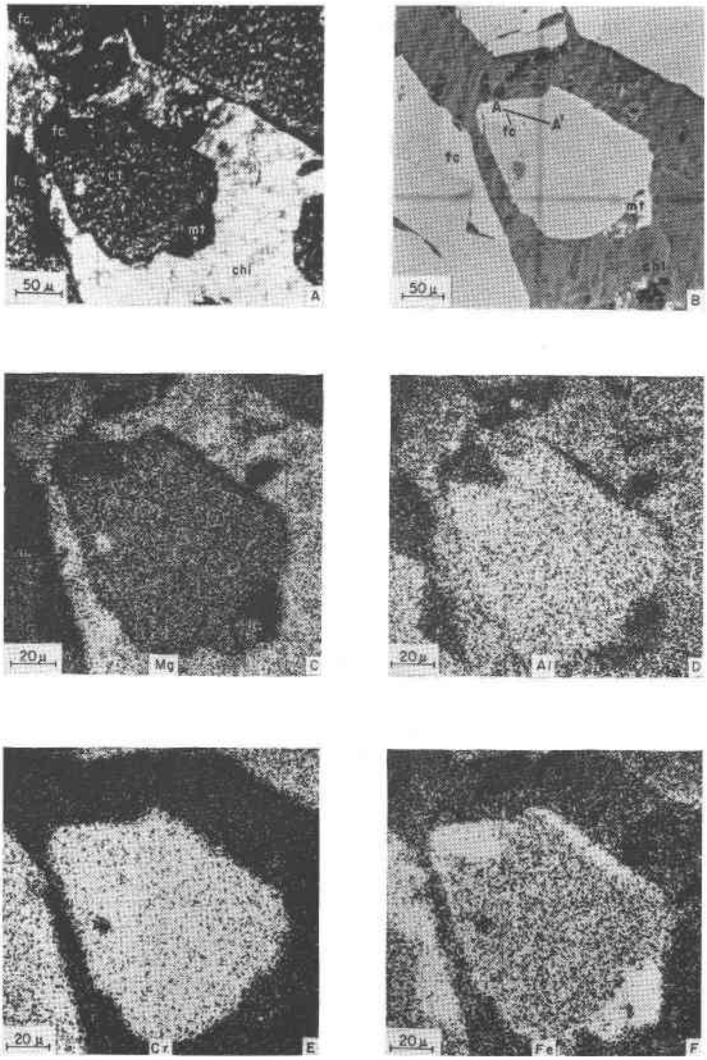

FIG. 2. A, Photomicrograph of 53EB-11, plane-polarized light. Cr = chromite; mt = magnetite; fc = ferritchromit; chl = chlorite. B, Photomicrograph of 53EB-11, reflected light. The replacement of chromite by ferritchromit along its margins is clearly evident. The smooth crystal outline of the original chromite grain is preserved indicating that the replacement is volume-for-volume. In B the textural differences between the magnetite, which forms as accretions on the borders of the ferritchromit and ferritchromit, which forms reentrants into the chromite grains, are easily seen. The step scan of 53EB-11 (Fig. 4) was taken along line A-A′ near the center of the photomicrograph. C, Beam scan photograph for Mg. D, Beam scan photograph for Al. E, Beam scan photograph for Cr. F, Beam scan photograph for Fe.

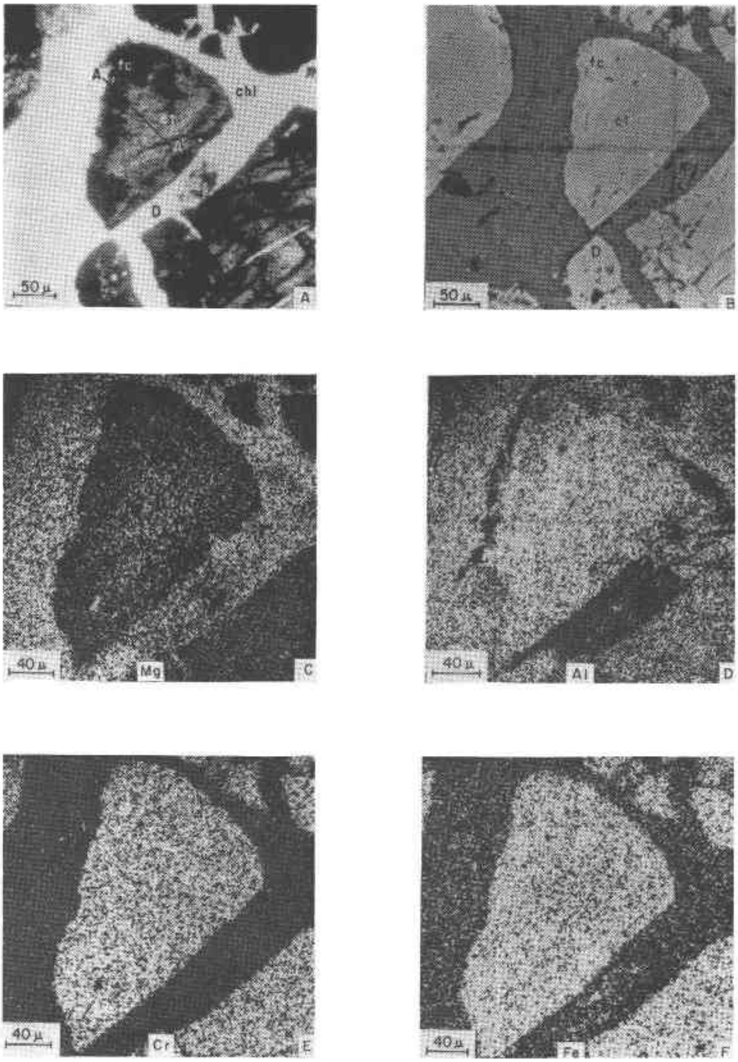

FIG. 3. A, Photomicrograph of 55WF-3, plane-polarized light. Step scan (Fig. 6) was made along line A-A′. The darkening of the chromite as ferritchromit is approached reflects increasing FeO and decreasing MgO. B, Photomicrograph of 55WF-3, reflected light. Ferritchromit is not so easily distinguished from its parent chromite as in 53EB-11 because the compositional difference between the two is less marked. C, Beam scan photograph for Mg. D, Beam scan photograph for Al. E, Beam scan photograph for Cr. F, Beam scan photograph for Fe.

having $a=8.38-8.39$.[1] The two phases were not resolved in diffractograms of 55WF-3, but a distinct broadening of the peaks asymmetrically toward the low angle side was observed. A cell dimension of $8.283 \pm .001$[2] was determined for the dominant phase. The failure to resolve two phases in the sample is in agreement with the optical observations and the chemical analyses (given below), which indicate a less distinct chemical separation of the two spinel phases in 55WF-3 than in 53EB-11.

X-ray diffraction analysis of the secondary silicates in both samples confirm that a 14 Å chlorite rather than serpentine is the alteration mineral present. The secondary silicate stratigraphically immediately below the chromite layer in 53EB-11 was shown to be serpentine (lizardite?) without detectable brucite. The absence of brucite has been verified only in the upper part of the serpentinized dunite layer but not for the whole layer. The presence of dolomite in 55WF-3 was also verified by X-ray diffraction.

CHEMICAL ANALYSES

Wet chemical analyses. The separation methods used to obtain cleaned chromite samples for wet chemical analyses, including heavy liquids, magnetic, and HF-leaching techniques, failed to separate the ferritchromit from the parent chromite; a ploished section of the cleaned separate contained as much ferritchromit as the whole sample. Magnetite, however, was completely removed. The number of silicate inclusions in both samples was unusually large for Stillwater chromites, and a fair number of these were apparently completely enclosed and retained in the separates. The amounts and proportions of impurities in the cleaned samples were estimated by grid counts, and subtracted from the chemical analyses.

Wet chemical analyses were done by J. I. Dinnin, employing the method he developed (1959), and are given in Tables 2 and 3. After silicate and carbonate impurities were subtracted good cation balance was obtained. The 53EB-11 concentrate calculated to 24.01 cations per 32 oxygen with a RO/R_2O_3 ratio of 0.999 and the 55WF-3 concentrate reduced to 23.99 cations per 32 oxygen, with a RO/R_2O_3 ratio of 0.991. Cation deficiencies of the maghemite type do not exist in the bulk sample, and cannot, therefore, be present in either the parent chromites or the ferritchromits. Total iron from the microprobe analysis of the separate phase was therefore partitioned as FeO and Fe_2O_3 assuming balanced spinels with $RO/R_2O_3=1$.

Microprobe analyses. Microprobe analyses were made by one of the authors (MB) using the M.A.C. model 400 microprobe. Quantitative analyses were done under constant conditions of 15 kV accelerating potential, 0.03 μA sample current, and a 20-second integration time. Unaltered chromites[3] from the Stillwater Complex were used as standards. All microprobe data were corrected for drift, background, and matrix absorption using computer methods (Beeson, 1967). The parent chromite and ferritchromit values in Figure 4 and Tables 2 and 3 were corrected for fluorescence by characteristic radiation as well as by using a modified Wittry correction.[4]

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[1] This value is approximate since it was determined using only the most distinct peak.

[2] Cell refinements were done by least squares using computer methods (Evans *et al.*, 1963). An internal quartz standard was used.

[3] J. I. Dinnin, analyst.

[4] J. Z. Frazer *et al.* (1966), Computer programs EMX and EMX2 for electron microprobe data processing. Univ. California, La Jolla, unpublished report SIO Ref. 66–14.

TABLE 2. CHEMICAL ANALYSES OF MINERALS IN 53EB-11

Oxide	Wet[a] chemical analysis	Corrected[b] wet analysis	Microprobe analyses				
			Parent[c] chromite	Ferrit-[c] chromit	Weighted[d] average	Magnetite	Chlorite
Cr_2O_3	45.7	46.5	47.1	42.0	46.4	4.6	1.5
Al_2O_3	17.1	16.5	18.6	3.1	16.4	1.0	21.0
Fe_2O_3	4.1	4.2	2.1[e]	22.4	4.9	62.4	n.d.
V_2O_3	0.76	0.76	n.d.	n.d.	n.d.	n.d.	n.d.
FeO	20.7	21.1	19.7	30.16	21.2	31.0	6.6
MgO	9.3	9.1	10.0	2.1	8.9	0.33	29.4
MnO	0.45	0.46	n.d	n.d.	n.d.	n.d.	n.d.
NiO	0.05	0.05	n.d.	n.d.	n.d.	n.d	n.d.
CoO	0.036	0.036	n.d.	n.d.	n.d.	n.d.	n.d.
ZnO	0.17	0.17	n.d.	n.d.	n.d.	n.d.	n.d.
TiO_2	0.85	0.87	0.71	1.04	0.76	n.d.	n.d.
CaO	0.07	—	n.d.	n.d.	n.d.	n.d.	n.d.
SiO_2	0.55	—	n.d.	n.d.	n.d.	n.d.	29.1
H_2O	0.54	—	n.d.	n.d.	n.d.	n.d.	12.0(est.)
CO_2	—	—	n.d.	n.d.	n.d.	n.d.	n.d.
Sum	100.4	100	98.2	100.80	98.56	99.33	99.6

[a] Analysis of cleaned ferritchromit-chromite concentrate by J. I. Dinnin.

[b] Impurities subtracted out based on proportions of identified silicate impurities in cleaned sample. The analysis represents a mixture of 87.5% chromite and 12.5% ferritchromit.

[c] Average of numerous points in area covered by photomicrographs.

[d] Based on weight fraction of chromite and ferritchromit determined from mode and assuming $\rho_{fc}=5.1$, $\rho_{ct}=4.5$.

[e] Total Fe of microprobe analysis partitioned between FeO and Fe_2O_3 assuming $RO/R_2O_3=1.0$.

Beam-scan photographs were taken to select appropriate areas for quantitative analysis and to provide a general picture of the alteration. The marked decrease of Mg and Al and increase of Fe in the ferritchromit areas, compared with the parent chromite areas of 53EB-11, is clearly shown in Figure 2 A–C. The Cr content in the ferritchromit remains essentially unchanged from the parent chromite, supporting the textural indication that the iron enrichment during alteration is the result of a volume-for-volume replacement of Mg and Al for iron and not a residual enrichment. The Cr distribution also clearly distinguishes ferritchromit from magnetite. The parent chromite-ferritchromit contacts are sharp within the limits of resolution of the beam-scan photographs.

Major element distributions in 55WF-3 (Fig. 3 C–F) are significantly different from those of 53EB-11. Mg and Fe are strongly zoned in both the parent chromite and ferritchromit, the Mg reaching a minimum and Fe a maximum near the edge of the ferritchromit away from the parent chromite. This is in marked contrast to the homogeneous distribution of Mg and Fe in 53EB-11. Al shows a less marked diminution in the ferritchromit but is not nearly so strongly zoned. The iron enrichment in the ferritchromit of this sample

TABLE 3. CHEMICAL ANALYSES OF MINERALS IN 55 WF-3

Oxide	Wet[a] chemical analysis	Corrected[b] wet analysis	Microprobe analyses				
			Parent[a] chromite	Ferrit[c] chromit	Weighted[d] average	Chlorite	Dolomite
Cr_2O_3	40.8	47.4	46.5	53.7	47.5	n.d.	n.d.
Al_2O_3	17.0	14.8	19.3	6.6	17.6	22.8	n.d.
Fe_2O_3	3.4	4.0	1.42[e]	8.4	2.4	n.d.	n.d.
V_2O_3	0.25	0.29	n.d.	n.d.	n.d.	n.d.	n.d.
FeO	24.5	28.5	21.1	32.1	22.6	4.8	2.9
MgO	6.9	3.6	9.2	1.68	8.2	31.3	20.1
MnO	0.28	0.33	n.d.	n.d.	n.d.	n.d.	n.d.
NiO	0.081	0.09	n.d.	n.d.	n.d.	n.d.	n.d.
CoO	0.060	0.09	n.d.	n.d.	n.d.	n.d.	n.d.
ZnO	0.19	0.20	n.d.	n.d.	n.d.	n.d.	n.d.
TiO_2	0.58	0.68	0.72	0.72	0.72	n.d.	n.d.
CaO	0.56	—	n.d.	n.d.	n.d.	n.d.	30.6
SiO_2	2.52	—	n.d.	n.d.	n.d.	30.2	n.d.
H_2O	1.18	—	n.d.	n.d.	n.d.	12.0(est.)	n.d.
CO_2	1.3	—	n.d.	n.d.	n.d.	n.d.	45.0(est.)
Sum	99.5	100.0	98.2	103.2	99.0	101.1	98.6

[a] Analysis of cleaned ferritchromit-chromite concentrate by J. I. Dinnin.

[b] Impurities subtracted out based on proportions identified silicate and carbonate impurities in cleaned sample. The analysis represents a mixture of 87.5% chromite and 12.5% ferritchromit.

[c] Average of numerous points in area covered by photomicrograph.

[d] Based on weight fraction of chromite and ferritchromit determined from mode and assuming $\rho_{fc}=5.0$ and $\rho_{ct.}=4.5$.

[e] Total iron from microprobe analysis partitioned between FeO and Fe_2O_3 assuming $RO/R_2O_3=1$.

could be partly the result of residual enrichment, since Cr is slightly enriched in the ferritchromit areas as well.

A plot of a step-scan analysis of 53EB-11 is given in Figure 4 (taken along line A-A′ shown in Figure 2B). The step scan shows both parent chromite and ferritchromit to be homogeneous, and the contact between them to be sharp, taking place essentially in a single 5-micron interval. If either magnesium or aluminum is more readily released from the spinel lattice during alteration, it is not evident from this scan. Also, as is to be expected from the cation balance, FeO and Fe_2O_3 increase sympathetically as MgO and Al_2O_3 decrease.

The step scan of 55WF-3 (shown plotted in Fig. 5 and made along line AA′ shown in Fig. 3-A), on the other hand, shows strong zoning of FeO and MgO in both the parent chromite and ferritchromit and of Al_2O_3, Fe_2O_3, and Cr_2O_3 in the ferritchromit. MgO and FeO are distinctly antithetic, the former decreasing and the latter increasing as the ferritchromit is approached. Al_2O_3, Cr_2O_3, and Fe_2O_3 are surprisingly constant until the contact between ferritchromit and parent chromite (as it would be visually placed) is reached,

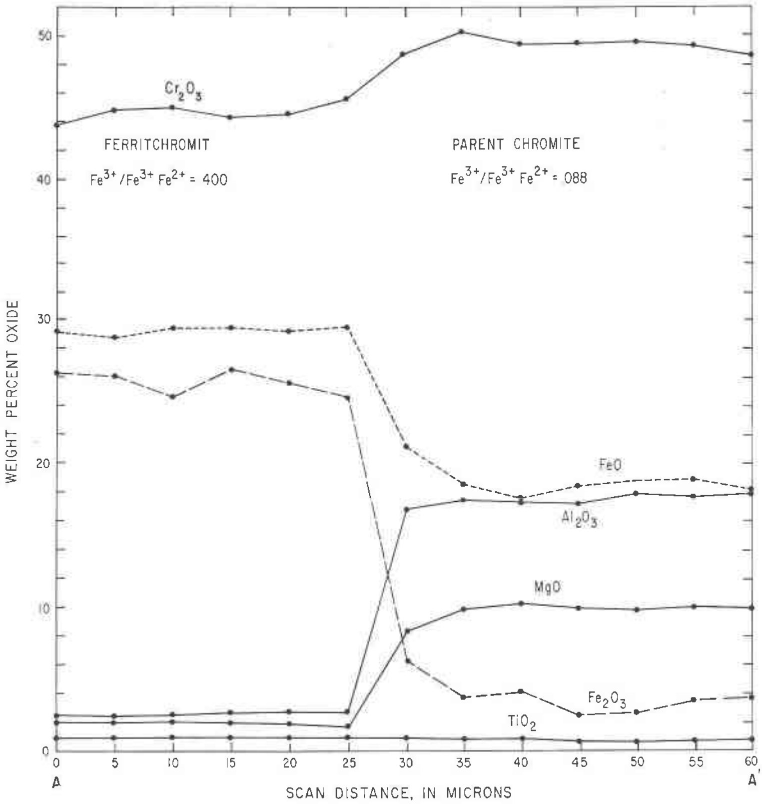

FIG. 4. Step scan across altered chromite in 53EB-11. Total iron of microprobe analysis partitioned between FeO and Fe_2O_3 assuming $RO/R_2O_3 = 1$.

where Al_2O_3 abruptly decreases and Fe_2O_3 and Cr_2O_3 abruptly increase. It is apparent that replacement of magnesium by ferrous iron in the spinel lattice precedes that of aluminum by ferric iron. This is contrary to the "expected mobility" of Mg and Al suggested by Golding and Bayliss (1968, p. 179) where they state that:

"Preferential mobility of Al over Mg might thus be expected as a result of the smaller size and location of the former in large octahedral holes as compared with the larger Mg ions in the smaller tetrahedral holes."

We conclude that position, bonding, and ionic size are not the controlling factors in the mobility of Mg or Al in the lattice, but rather that the availability of Fe^{+2} or Fe^{+3} fixes the amount of bivalent Mg and trivalent Al that are replaced. We suppose that the $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ ratio is fixed in turn as a result of P_{O_2} during alteration.

The cause of the sharp inflection of each element in the ferritchromit of 55WF-3 near its contact with chromite is not apparent. Neither magnetite nor especially iron-rich ferritchromit is visible along the contact. (Such an area below the polished surface would, of course, not be optically detectable.) The deflection is not spurious, since it appeared on separate scans along the same line. The general zoning trends are, in general, maintained if projected across the compositional spikes.

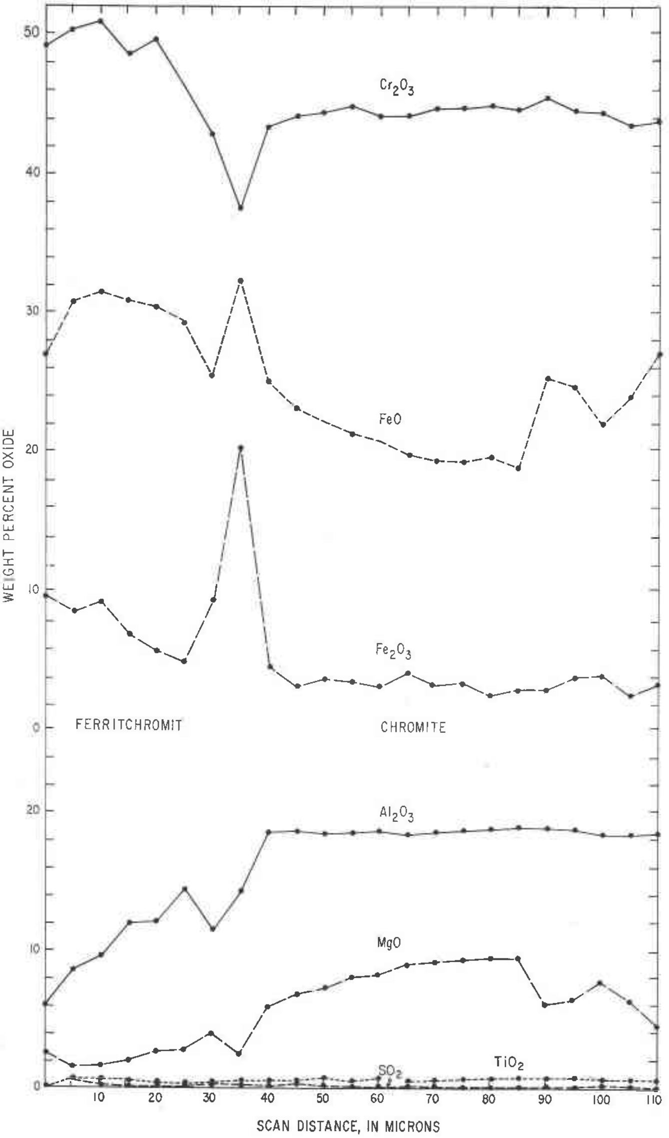

FIG. 5. Step scan across altered chromite in 55WF-3. Total iron of microprobe analysis partitioned between FeO and Fe$_2$O$_3$ assuming RO/R$_2$O$_3$ = 1.

Correlation of microprobe and wet analyses. As a test of internal consistency, a weighted average of ferritchromit and parent chromite compositions was made for both samples, using appropriate weight fractions based on the mode and estimated densities. The close correspondence between the corrected wet analysis and the weighted average of the microprobe analysis for 53EB-11 (Table 2) supports the assumptions in the impurity correction as well as substantiating the accuracy of microprobe analyses and mode.

A similar comparison for 55WF-3 (Table 3) is very much less satisfying. However, since both the parent chromite and the ferritchromit in this sample are strongly zoned, especially in MgO and FeO, and since the microprobe analyses used were intended to represent the initial chromite composition and not the average of the remaining chromite, this poorer agreement is perhaps not surprising. The mode for this sample, too, is less reliable, because the ferritchromit and chromite are more difficult to distinguish in polished section.

CHEMISTRY OF THE ALTERATION

Material transfer equations have been written for one sample, 53EB-11, in an attempt to show what changes occurred in the chromitite layer during its alteration. These equations are only intended to show the secondary phases, the primary phases, and the material transfer that might have taken place; nothing is inferred about the actual reactions that produced the alteration.

Several rigid restrictions are placed on these equations by the data presented. These are as follows:

1. The volume of the ferritchromit must be nearly equal to or less than the volume of the chromite it replaced. It is clear from the retention of the primary crystal outlines of the chromite after alteration that this was a volume-for-volume replacement. A volume reduction of 2 and 3 percent could be accounted for by the small chlorite inclusions in the ferritchromit where these occur, but they are rather rare.

2. The ratios of the volumes of chlorite, ferritchromit, and magnetite, the secondary phases, are fixed by the mode, these being: chlorite 19.5 percent, ferritchromit 12.5 percent, and magnetite 2.5 percent.

3. The chemical compositions of all the secondary phases, and that of the parent chromite, are fixed by the analyses Table 2. In 53EB-11, both ferritchromit and parent chromite are homogeneous, and the average of the several areas analyzed with the electron microprobe adequately represents the composition of the parent chromite and ferritchromit. We conclude, therefore, that our initial chromite composition for this sample, at least, is correct. The chromium content is nearly constant in the two phases; that is, little is lost or gained from the area of concern, which also appears reasonable.

4. An additional restriction is that the mineralogy and compositions of the primary silicate phase (or phases) be consistent with those in other similar but unaltered chromitite zones in the Stillwater Complex. This phase was judged to have most likely been olivine of about Fo_{85}. In our experience, the absence of dolomite among the alteration products of

53EB-11 suggests no plagioclase was present in the unaltered sample; indeed, very little feldspar is present in fresher smaples in the area from which this sample was collected. Compositions of all required phases and cation ratios for chromite, ferritchromit, and magnetite are given in Tables 2 and 4 respectively.

Volume-for-volume replacement for the whole outcrop area is suggested by the field relations. The presence of thin chromitite layers like this one that can be correlated for miles on strike, in and out of partially serpentinized areas, and which retain their primary cumulus texture, does not permit large volume expansions to have occurred. If expansion of the dunite layers above and below the chromitite layers had taken place during alteration, one would expect a physical disruption or separation of the cumulus textures of the chromitite. However, no such disruption was seen in the serpentinized areas. Assuming then that the volume remained constant during the alteration, the following material transfer equation results.

$$\underset{\substack{M = 1527.4,\ D = 4.5,\ V = 339.4\\(1485.0\text{ cc})}}{\overset{\text{chromite}}{35[(\overset{2+}{\mathrm{Fe}}_{.52}\mathrm{Mg}_{.48})(\mathrm{Cr}_{1.22}\mathrm{Al}_{.72}\overset{3+}{\mathrm{Fe}}_{.06})\mathrm{O}_4]}} + \underset{\substack{M = 1192.5,\ D=3.3,\ V = 361.4\\(2452.7\text{ cc})}}{\overset{\text{olivine}}{54.3[(\mathrm{Mg}_{1.7}\mathrm{Fe}_{.3})\mathrm{SiO}_4]}}$$

$$+ \underbrace{40.8\mathrm{H_2O} + 17.5\mathrm{Fe_2O_3} + 1.8\mathrm{FeO} + 0.5\mathrm{Cr_2O_3} + 2.0\mathrm{Al_2O_3}}_{\text{introduced}} \rightarrow$$

$$\underset{\substack{M = 1752.4,\ D=5.1,\ V=343.6\\(1460.3\text{ cc})}}{\overset{\text{ferritchromit}}{34[(\overset{2+}{\mathrm{Fe}}_{.88}\mathrm{Mg}_{.12})(\mathrm{Cr}_{1.21}\overset{3+}{\mathrm{Fe}}_{.65}\mathrm{Al}_{.14})\mathrm{O}_4]}} + \underset{\substack{M = 1834.1,\ D = 5.15,\ V = 356.1\\(293.7\text{ cc})}}{\overset{\text{magnetite}}{6.6[(\overset{2+}{\mathrm{Fe}}_{.99}\mathrm{Mg}_{.01})(\overset{3+}{\mathrm{Fe}}_{1.75}\mathrm{Cr}_{.21}\mathrm{Al}_{.09})\mathrm{O}_4]}}$$

$$+ \underset{\substack{M = 1151,\ D = 2.6,\ V = 442.7\\(2257.9\text{ cc})}}{\overset{\text{chlorite}}{5.1[(\mathrm{Mg}_{8.38}\mathrm{Cr}_{.23}\mathrm{Al}_{2.30}\mathrm{Fe}_{1.06})(\mathrm{Al}_{2.43}\mathrm{Si}_{5.57})\mathrm{O}_{20}(\mathrm{OH})_{16}]}} + \underbrace{62.2\mathrm{MgO} + 25.9\mathrm{SiO_2}}_{\text{removed}}$$

If the constant volume assumption is correct, it is necessary to introduce large amounts of iron and to remove very large amounts of Mg and Si. The material exchanged amounts to about 30 percent by volume of the original rocks. A possible source for the iron is readily available from serpentinized dunites above and below the 6-inch-thick chromitite zone from which this sample was taken, but no data on the dunite are available to either prove or disprove it as a source of the iron.

If constant silicon is assumed, the following mineral transfer equation results.

$$\underset{\substack{M\,=\,1527.4,\ D\,=\,4.5,\ V\,=\,339.4\\(1485.0\text{ cc})}}{\overset{\text{chromite}}{35[(\mathrm{Fe}^{2+}_{.52}\mathrm{Mg}_{.48})(\mathrm{Cr}_{1.22}\mathrm{Al}_{.72}\mathrm{Fe}^{3+}_{.06})\mathrm{O}_4]}} + \underset{\substack{M\,=\,1192.5,\ D\,=\,3.3,\ V\,=\,361.4\\(1282.9\text{ cc})}}{\overset{\text{olivine}}{28.4[(\mathrm{Mg}_{1.7}\mathrm{Fe}_{.3})\mathrm{SiO}_4]}} +$$

$$\underbrace{40.8\mathrm{H_2O} + 23.4\mathrm{Fe_2O_3} + \mathrm{Cr_2O_3} + 2.0\mathrm{Al_2O_3}}_{\text{introduced}} \rightarrow$$

$$\underset{\substack{M\,=\,1752.4,\ D\,=\,5.1,\ V\,=\,343.6\\(1460.3\text{ cc})}}{\overset{\text{ferritchromit}}{34[(\mathrm{Fe}^{2+}_{.88}\mathrm{Mg}_{.12})(\mathrm{Cr}_{1.21}\mathrm{Fe}^{3+}_{.65}\mathrm{Al}_{.14})\mathrm{O}_4]}} + \underset{\substack{M\,=\,1834.1,\ D\,=\,5.15,\ V\,=\,356.1\\(293.7\text{ cc})}}{\overset{\text{magnetite}}{6.6[(\mathrm{Fe}^{2+}_{.99}\mathrm{Mg}_{.01})(\mathrm{Fe}^{3+}_{1.75}\mathrm{Cr}_{.21}\mathrm{Al}_{.04})\mathrm{O}_4]}} +$$

$$\underset{\substack{M\,=\,1151,\ D\,=\,2.6,\ V\,=\,442.7\\(2257.9\text{ cc})}}{\overset{\text{chlorite}}{5.1[(\mathrm{Mg}_{8.38}\mathrm{Cr}_{.23}\mathrm{Al}_{2.3}\mathrm{Fe}_{1.06})(\mathrm{Al}_{2.43}\mathrm{Si}_{5.57})\mathrm{O}_{20}(\mathrm{OH})_{16}]}} + \underbrace{18\mathrm{MgO}}_{\text{removed}}$$

The assumption of constant silicon requires the introduction of far larger amounts of iron but removal of less MgO. An additional, but extremely sticky requirement is that the volume of the silicate phase must double.

The limits established by the mode and compositions of the various phases does not permit a material transfer equation to be written in which only water is introduced, but requires that relative amounts of the components be changed.

This kind of exercise could of course also be carried out for 55WF-3, but the added complications of determining initial composition for the parent chromite and reliable mode of the rock would make the results of doubtful value. Qualitatively, the results are similar to those above; an assumption of constant volume requires the transport of a great deal of material, and an assumption of constant silicon requires a very large volume change.

CONCLUSIONS

The volume-for-volume alteration of chromite to ferritchromit in our samples appears to be genetically related to the formation of chlorite; the Al released by the chromite being taken up by the silicate. All of the ten samples from the Stillwater Complex which contain ferritchromit also contain chlorite, but this mineral was identified in only three other chromitites. Reexamination of two of these revealed definite ferritchromit in one and suspected ferritchromit in the other.

It is important that ferritchromit be carefully looked for in chromite being considered for analysis because even small amounts of it can seriously affect the composition assigned to the magmatic spinel, especially

Table 4. Cation Ratios for Chromites and Ferritchromits 53EB-11 and 55WF-3

	$\frac{Mg}{Mg+Fe^{2+}}$	$\frac{Fe^{2+}}{Mg+Fe^{2+}}$	$\frac{Cr}{Cr+Al+Fe^{3+}}$	$\frac{Al}{Cr+Al+Fe^{3+}}$	$\frac{Fe^{3+}}{Cr+Al+Fe^{3+}}$	$\frac{Fe^{3+}}{Fe^{3+}+Fe^{2+}}$
53EB-11						
Corrected wet analysis	0.435	0.565	0.619	0.328	0.053	0.152
Parent chromite	.475	.525	.613	.361	.026	.088
Ferritchromit	.112	.899	.619	.068	.313	.400
Weighted[a] average	.428	.572	.614	.324	.062	.173
55WF-3						
Corrected wet analysis	0.184	0.816	0.647	0.301	0.052	0.112
Parent chromite	.437	.563	.607	.375	.018	.057
Ferritchromit	.085	.915	.751	.137	.112	.191
Weighted[a] average	.393	.607	.625	.345	.030	.087

[a] Based on weight fraction of chromite determined from mode assuming $\rho_{fc}=5.1$ and 5.0 for 53EB-11 and 55WF-3 respectively and $\rho_{ct}=4.5$ for both samples.

as it relates to the oxidation ratio. In Table 4, for example, the values of oxidation ratios of both the primary magmatic chromites are less than half of the values calculated from the bulk wet chemical analyses.

The associations of chromite with olivine and ferritchromit with chlorite, and the unusual chemical composition of the ferritchromit, lends additional support to Thayer's contention (1956) that most chrome ores are magmatic and not hydrothermal.

Serpentinization is considered by some workers (*e.g.*, Thayer, 1966) to take place at nearly constant volume; others (*e.g.*, Hostetler *et al.*, 1966; Page, 1967) maintain that it is more nearly a constant composition process. Although the chemical data gathered for 53EB-11 is unusually complete, it provides no unique answer to the constant volume-constant composition problem.

Textural relations and field evidence, however, suggest constant volume. Within the chromitite layers no disturbance of the primary cumulate texture is observed, and, in addition, the preservation of the broader structural and stratigraphic relations, in which thin chromitite layers may be traced in and out of areas of serpentinization without detectable disturbance or disruption, will not permit the volume increase of about 25–48 percent that Hostetler *et al.* (1966) calculate.

The absence of brucite in the serpentine underlying 53EB-11 may be significant; Hostetler *et al.* (1966) have shown that volume change decreases as the percentage of brucite decreases, though they still require a volume change of about 25 percent with no brucite. Constant composition processes may be dominant in Alpine peridotites, where brucite is generally abundant. Brucite, therefore, may prove to be a key mineral in determining the serpentinization mechanism, though more work is needed.

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