CHROMITE FROM "EQUILIBRATED" CHONDRITES

KENNETH G. SNETSINGER, KLAUS KEIL AND T. E. BUNCH, Space Sciences Division, Ames Research Center, NASA, Moffett Field, California.

Abstract

Electron microprobe analysis of chromite in seven "equilibrated" chondrites shows that, within a given meteorite, chromite grains are remarkably similar in composition; no zoning occurs. From meteorite to meteorite, however, the mineral has the narrow compositional range (weight percents) Cr$_2$O$_3$ 54.6-57.0, Al$_2$O$_3$ 5.2-6.3, TiO$_2$ 2.08-2.98, FeO 30.5-33.9, MgO 1.54-2.48, MnO 0.65-1.05, V$_2$O$_5$ 0.65-0.77, which corresponds to the average structural formula \((\text{Fe}_{0.90}\text{Mg}_{0.10})\text{(Cr}_{2.40}\text{Al}_{0.60}\text{Fe}_{0.00}\text{Ti}_{0.02})\text{O}_{4.20}\). These chondritic chromites are higher in iron than most terrestrial examples, and approach the theoretical composition \((\text{FeCr}_{2}\text{O}_{4})\) of chromite. Titanium contents are also higher than the average for terrestrial chromite, and several considerations indicate that the element is in the structure of the mineral and not present as rutile or ilmenite inclusions. Aluminum is, on the other hand, deficient compared to most terrestrial chromites, and this is probably due to presence of plagioclase in chondrites, most of the aluminum being taken up by the feldspar.

Although the range in composition of chromite in the chondrites studied is slight, amounts of oxides present in the mineral do appear to show a relation to the chemistry of the meteorites: chromite from the H-group chondrites tends to be higher in chromium and aluminum than L- or LL-group chromites, and chromite in H-group chondrites is lower in titanium than L- or LL-group chromites. Iron and magnesium show, respectively, an increase and a decrease in amount as one passes from the H- to L- to LL-group chromites. Because this iron and magnesium variation has the same trend as found in the olivines and pyroxenes in H-, L-, and LL-group chondrites, it is suggested that, in the examples studied, chromite is in equilibrium with the ferromagnesian silicates, a situation which may be due to (1) equilibration during contemporaneous crystallization of the iron-magnesium silicates and the chromite or (2) equilibration during contemporaneous metamorphism of silicates and chromite.

Introduction

Chromite is a ubiquitous constituent of meteorites but, owing to its presence in small amounts, determination of chemical properties by traditional methods presents difficulties. Thus, although abundant compositional data exist for terrestrial examples (e.g., Stevens, 1944; Thayer, 1956; Weiser, 1966), relatively few chemical studies of meteoritic chromite have been attempted. Twenty-one analyses are available in the literature, and of these, seventeen are earlier ones performed on chromite separated from octahedrites, pallasites, and chondrites (Tassin, 1908). More recently, however, Stulov (1960) has analyzed chromite from the Sikhote-Alin octahedrite using X-ray fluorescence techniques, while the electron microprobe has been put to use in analysis of chromite in the Dosso chondrite (Jérémie et al., 1964), the Steinbach siderophyre (Dörfler et al., 1965), and the Farmington chondrite (Buseck and Keil, 1966).

1 Portions of this paper were first presented at the 29th Annual Meeting of the Meteoritical Society, Washington, D. C., November 3-5, 1966.
Chromite is present in such small amounts in chondrites—the mineral averages but 0.3 weight percent of these meteorites (Keil, 1962)—that the electron probe technique provides the only practical approach for obtaining chemical data. In the present paper electron microprobe analyses of chromites from seven "equilibrated" chondrites are reported, and the data indicate that the composition of the chromite has a relation to the chemistry of the chondrites.

The terms "equilibrated" and "unequilibrated" were first proposed by Dodd and Van Schmus (1965) for chondrites whose olivines and pyroxenes are, respectively, homogeneous, and strongly-zoned. "Equilibrated" is, however, misleading, because even the most highly "equilibrated" chondrites contain metallic nickel-iron with strong grain-boundary compositional gradients, indicating disequilibrium. Because of lack of a better term the designation "equilibrated" chondrites is retained in the present paper to describe meteorites containing homogeneous olivines and pyroxenes. Van Schmus and Wood (1967) propose a subdivision of the major H-, L-, and LL-group chondrites¹ on the basis of their degree of metamorphism as judged by the presence of primary glass, distinctness of chondrules, homogeneity of silicates, etc., into 30 possible types (e.g., H1-H6, L1-L6), 20 of which are known. Most of the meteorites studied here belong to the most highly "equilibrated" groups of Van Schmus and Wood, and are the following: Bath (H4); Hessle (H5); Allegan (H5); Modoc 1 (L6); Kyushu (L6); Severukovo (L; unclassified as to textural group); and Cherokee Springs (LL6).

EXPERIMENTAL PROCEDURES

A number of analytical procedures used in this study appear not to have been previously attempted and, accordingly, they are described in some detail.

An ARL-EMX electron microprobe was employed; iron, chromium, magnesium, and aluminum values were obtained by comparison to a wet-chemically analyzed terrestrial chromite similar in composition to the meteoritic ones, and for manganese and titanium, pure Mn and synthetic stoichiometric TiO₂ were used as standards.

Particular attention was directed to evaluation of the terrestrial chromite prior to its use as a standard. Sequential point analyses with the electron probe revealed no zoning of the standard mineral grains, but slight compositional variation from grain to grain was noted. Accord-

¹ The distinction of H-, L-, and LL-group chondrites is made largely on the basis of ferrous, metallic, and total iron contents; ferrous iron increases from H- to L- to LL-groups, while metallic and total iron both decrease (Urey and Craig, 1953; Keil and Fredriksson, 1964).
ingly, all grains in the standard mount (these numbered seventeen) were
analyzed with the electron probe and one grain closest to the average
composition for all the grains was chosen as standard. The composition
of this standard grain was not, however, precisely that of the whole
chromite as determined by the wet chemical analysis, and correction for
this was made in calculating analytical results for the meteoritic chro-
mites. In addition, analytical values for the standard were checked by
using the grain in duplicate analysis of several terrestrial chromites
whose compositions are well known; magnesium and iron contents were
found to be slightly in error, and adjustment was made for this in
analysis of the meteoritic chromites. As a result of such evaluation,
some data are available regarding accuracy of analysis of the meteoritic
chromites, and these, expressed as weight percentages of the amounts of
oxides present, are: \( \text{Cr}_2\text{O}_3 \pm 0.9\% \); \( \text{FeO} \pm 1.1\% \); \( \text{MgO} \pm 3.3\% \); \( \text{Al}_2\text{O}_3 \pm 8.1\% \). Precision is from 0.5 to 5 percent of the amounts of oxides present,
depending on concentration and element: it was less than 1 percent for
concentrations greater than 10 weight percent; 1–3 percent for amounts
between 3 and 10 weight percent; and up to 5 percent for concentrations
less than 3 weight percent.

Because AlK\(_\alpha\) radiation coincides with fourth order CrK\(_\beta\) radiation,
pulse height selection was used in the determination of aluminum. It
may, however, be of interest to point out that pulse height selection is
not the only approach in this case: it was found that if the accelerating
voltage of the electrons is kept below the level at which excitation of
chromium K series occurs, results are in good agreement with those
obtained by pulse height selection, provided beam current is increased to
maintain adequate counting rates.

X-ray intensities were adjusted to take account of drift, detector and
amplifier deadtime, background, mass absorption, fluorescence, and
atomic number. Philibert's (1963) equation, as modified by Duncumb
and Shields (1966), and Heinrich's (1966) mass absorption coefficients
were used in calculating the mass absorption corrections.

Secondary fluorescence of chromium by FeK\(_\alpha\) was determined empiri-
cally in the following way: a chemically analyzed terrestrial chromite
with an Fe/Cr ratio and an average atomic number very close to the
meteoritic ones was analyzed with the electron probe for chromium and
iron using the chromite standard described above, and after all correc-
tions except fluorescence and atomic number had been applied, the
amount of Cr in excess of the true (wet-chemical) value was ascribed to
fluorescence (the difference in average atomic number of standard and
sample was, in this instance, so small as to be negligible). The correction
so obtained was applied to each meteoritic chromite. Incidental to this,
it should be pointed out that the empirically determined excess over the true value of elemental Cr resulting from fluorescence of Cr by Fe was 1.33 weight percent at the chromium and iron levels encountered in the chondritic chromites and, using Wittry's (1962) theoretical formulas, a quite comparable value for the fluorescence correction was obtained: 1.08 weight percent Cr. Considering that this theoretical calculation involved assuming that the chromite was made up of Fe, Cr, and a third element having a mass absorption coefficient equal to that of iron (Wittry, 1962, pp. 12–13), a situation hardly comparable to the actual one, agreement with the empirical determination is quite good. This suggests that Wittry's (1962) formulas for binary systems may, with some confidence, be extended to ternary systems, at least in the case of the elements considered here.

Because the wavelength of CrKα and FeKα approach the absorption edge of titanium, fluorescence of Ti by these elements was suspected—especially so in view of the strong fluorescence of Ti by Fe in stainless steel reported by Birks (1959, p. 114), and fluorescence of Ti by Fe in ilmenite noted by Reed (1965). Application of Wittry's (1962) formulas showed, however, that the effect would be very slight with the chromites, and this was verified empirically by using an approach similar to the one just outlined. The excess of Ti over the true value in an analyzed chromite roughly similar in composition to the meteoritic ones was 0.04 percent at a titanium level of 0.96 percent—a negligible excess.

The effect of atomic number difference between samples and standards was estimated by measuring iron in FeS₂ of known composition using pure Fe as a standard; after all corrections were made, the factor necessary to obtain the proper iron value for FeS₂ was assumed due to atomic number difference, and this factor was arbitrarily applied to the meteoritic chromites proportionally according to the difference in atomic number between the chromites and the standards used in their analysis. Because the average atomic number of the chromite standard was very similar to the average atomic numbers of the analyzed meteoritic chromites, atomic number corrections were almost negligible in the case of Fe, Cr, Mg, and Al. For Mn and Ti the corrections amounted to less than one percent of the amounts present.

Several writers (Wright and Lovering, 1965; Carmichael, 1967) have drawn attention to coincidence of TiK₂, with VKα. Pulse height selection is of no use in eliminating this interference: VKα and TiK₂ radiations are nearly identical in wavelength, and therefore in energy. Accordingly, for analysis of V, a special method was devised. Briefly, the procedure involves determining the ratio of intensity of TiKα to the intensity of TiK₂, the latter being measured at the wavelength of VKα; pure
rutile is used is a standard for this determination. Then titanium and vanadium are measured on the unknown chromite, the TiKα/TiKβ ratio obtained from rutile being used to correct the VKα intensity for interference from TiKβ. Corrections for continuous background are made by measuring a vanadium- and titanium-free sample that has an average atomic number close to the chromite and rutile. This procedure is considerably more involved than the above would suggest, and full discussion of it is the subject of a separate paper in preparation by Snetsinger, Bunch and Keil. Quite reliable results are obtained; analysis of a titanium-bearing chromite standard with a known vanadium content gave excellent agreement with the wet-chemical value for vanadium in the standard. In addition, values for vanadium in two of the meteoritic chromites, obtained with the laser microprobe (Snetsinger and Keil, 1967), agree closely with values obtained by the above method.

To eliminate any possible influence of terrestrial oxidation on the chromites, only meteorites seen to fall were selected for analysis. An average of five chromite grains per meteorite were analyzed; only grains larger than 15 microns in diameter were investigated, in order to avoid grain boundary and secondary fluorescence effects.

**Chemical Properties**

The analyses of the chromites, and structural formulas on the basis of 32 oxygens per unit cell, are given in Table 1. Assuming that ferrous iron may be present in octahedral as well as tetrahedral formula sites, as with some of the inverse spinels, sufficient iron has been assigned to the tetrahedral group to make its sum 8.0, and the remainder given to the octahedral cation position. Titanium is assumed to be in octahedral coordination (as it is in ulvöspinel), and magnesium, which conceivably could be in both 6- and 8-fold coordination with oxygen, is assumed to behave tetrahedrally.

These chromites are higher in iron than most terrestrial examples, and may be classified as ferrochromites according to the usage suggested by Stevens (1944); they approach the composition (FeCr2O4) of ideal chromite. Serial point analyses with the electron probe fail to reveal presence of zoning; chromite grains within one given meteorite are remarkably similar in composition.

The average TiO2 value for the analyses of terrestrial chromites

1 Structural formula calculations were done with the computer program devised by Jackson et al. (1967).

2 Nearly all chromite analyses presently in the literature have been done on chromites from chromitites or chromite-rich ore; thus a rather restricted environment is represented and it may be misleading to consider that the average of the analyses recorded by Stevens (1944) is a correct one for terrestrial chromites as a whole.
### Table 1. Analyses and Structural Formulas of Chromites from “Equilibrated” Chondrites

<table>
<thead>
<tr>
<th>Group Meteorite</th>
<th>H Bath</th>
<th>H Hessle</th>
<th>H Allegan</th>
<th>L Modoc 1</th>
<th>L Kyushu</th>
<th>L Sevrukovo</th>
<th>LL Cherokee Springs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂O₃</td>
<td>56.4</td>
<td>57.0</td>
<td>56.5</td>
<td>56.5</td>
<td>55.9</td>
<td>54.6</td>
<td>54.8</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>6.2</td>
<td>5.9</td>
<td>6.3</td>
<td>5.2</td>
<td>5.4</td>
<td>5.2</td>
<td>5.2</td>
</tr>
<tr>
<td>V₂O₃</td>
<td>0.70</td>
<td>0.65</td>
<td>0.71</td>
<td>0.70</td>
<td>0.77</td>
<td>0.70</td>
<td>0.74</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.24</td>
<td>2.21</td>
<td>2.08</td>
<td>3.06</td>
<td>3.13</td>
<td>3.09</td>
<td>3.98</td>
</tr>
<tr>
<td>FeO</td>
<td>30.5</td>
<td>31.3</td>
<td>32.0</td>
<td>31.8</td>
<td>32.5</td>
<td>32.6</td>
<td>33.9</td>
</tr>
<tr>
<td>MgO</td>
<td>2.48</td>
<td>2.35</td>
<td>2.31</td>
<td>1.79</td>
<td>1.79</td>
<td>2.02</td>
<td>1.54</td>
</tr>
<tr>
<td>MnO</td>
<td>0.93</td>
<td>0.96</td>
<td>1.05</td>
<td>0.74</td>
<td>0.76</td>
<td>0.65</td>
<td>0.68</td>
</tr>
<tr>
<td>Totals</td>
<td>99.45</td>
<td>100.37</td>
<td>100.95</td>
<td>99.79</td>
<td>100.25</td>
<td>98.76</td>
<td>100.84</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Structural Formula</th>
<th>Cations</th>
<th>Weight Percent Fe₂O₃ (Calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bath</td>
<td>(Fe₀.₇₃⁺Mg₁.₉₅Mn₀.₂₂)(Cr₁₂.₇₄Al₂.₄₉V₀.₁₆Fe₀.₄₇⁺Ti₀.₄₈)O₂₂</td>
<td>24.04</td>
<td>0.56</td>
</tr>
<tr>
<td>Hesse</td>
<td>(Fe₀.₇₇⁺Mg₁.₀₉Mn₀.₂₃)(Cr₁₂.₉₀Al₁.₇₈V₀.₁₆Fe₀.₆₇⁺Ti₀.₄₇)O₂₂</td>
<td>24.07</td>
<td>0.56</td>
</tr>
<tr>
<td>Allegan</td>
<td>(Fe₀.₇₈⁺Mg₀.₉₅Mn₀.₂₆)(Cr₁₂.₆₃Al₂.₁₀V₀.₁₆Fe₀.₇₉⁺Ti₀.₄₄)O₂₂</td>
<td>24.12</td>
<td>1.67</td>
</tr>
<tr>
<td>Modoc 1</td>
<td>(Fe₀.₇₅⁺Mg₀.₇₅Mn₀.₁₅)(Cr₁₂.₇₅Al₁.₇₅V₀.₁₆Fe₀.₄₅⁺Ti₀.₆₅)O₂₂</td>
<td>23.98</td>
<td>0.00</td>
</tr>
<tr>
<td>Kyushu</td>
<td>(Fe₀.₆₀⁺Mg₀.₇₆Mn₀.₁₈)(Cr₁₂.₅₈Al₁.₈₂V₀.₁₃Fe₀.₇₁⁺Ti₀.₆₇)O₂₂</td>
<td>24.0₁</td>
<td>0.00</td>
</tr>
<tr>
<td>Sevrukovo</td>
<td>(Fe₀.₉₂⁺Mg₀.₈₅Mn₀.₁₆)(Cr₁₂.₅₃Al₁.₇₈V₀.₁₆Fe₀.₄₉⁺Ti₀.₆₇)O₂₂</td>
<td>24.0₈</td>
<td>1.00</td>
</tr>
<tr>
<td>Cherokee Springs</td>
<td>(Fe₇.₁₉⁺Mg₀.₆₃Mn₀.₁₆)(Cr₁₂.₃₃Al₁.₇₅V₀.₁₇Fe₀.₈₉⁺Ti₀.₈₃)O₂₂</td>
<td>24.0₁</td>
<td>0.00</td>
</tr>
</tbody>
</table>
given by Stevens (1944) is 0.45 weight percent, whereas the chondritic chromites contain much more of this constituent. Two considerations suggest that titanium is not bound up in rutile or ilmenite included in the meteoritic chromites. First, sequential point analyses with the electron probe show very little variability of titanium, and fail to reveal high-titanium sample areas. Second, during careful microscopic inspection of the chromite grains, using oil immersion at a magnification of 1280 times, no rutile or ilmenite was found. It appears that the titanium is present in the structure of the chromite. This is in contrast to many terrestrial examples, for the latter often show exsolved lamellae of ilmenite and, less commonly, rutile, even though the total Ti content of terrestrial chromites is less than that of meteoritic ones. Perhaps some feature of environment is responsible for the difference.

The chondritic chromites have lower aluminum contents (about 6 percent Al₂O₃) than terrestrial ones: the average of the analyses of terrestrial chromites cited by Stevens (1944) is 15.6 percent Al₂O₃. This difference is most probably due to presence of 5–10 percent oligoclase in the chondrites, aluminum having been taken up in part by the feldspar, whereas terrestrial chromite-rich rocks are generally feldspar-free ultrabasic types, in which chromite is commonly the only mineral that can accommodate aluminum.

The high iron and low magnesium as compared with terrestrial chromites is considered due to greater availability of iron in chondritic meteorites. Occurrence of appreciable vanadium in the chromites is of interest; this metal is apparently concentrated in chromite, occurring in only minor amounts in other phases present in chondritic meteorites.

Despite the fact that all major oxides were determined, cation summations of a number of the analyzed chromites are in excess of the 24.00 cations found in ideal chromite. The discrepancy may in these examples be due to presence of a small amount of ferric iron. It was initially planned to estimate ferrous-ferric iron ratios by measuring the wavelength shift of FeLα (Fischer, 1964) or the intensity ratio of FeLα₁,₂ to FeLβ₁ (Andersen, 1966). But the amounts of ferric iron necessary to reduce cation summations to 24.00 are so small (Table 1) as to be immeasurable by either of these methods.

1 Stevens' analyses were recalculated by him to eliminate any titanium which may have been present as ilmenite.
2 Weiser (1966) has, however, recorded a few terrestrial examples of chromites very low in alumina and therefore closer in composition to ferrochromites than the present examples.
3 Ferric iron was calculated by subtracting various amounts of FeO from the FeO values, converting the amount subtracted to the equivalent Fe₂O₃ and repeatedly calculating the structural formulas until they totalled 24.00±0.01 cations.
It appears that some of the earlier analyses of meteoritic chromite may be in error, particularly as regards aluminum content. Eberhardt (1882) reported 28.50 percent Al$_2$O$_3$ in chromite from the Sevrukovo chondrite while we find only 5.24 percent, and Tassin's (1908) analysis of Allegan chromite gives 12.38 percent Al$_2$O$_3$, whereas our analysis shows but 6.33 percent.

**UNIT CELL**

Sufficient chromite for X-ray work was obtained by treating several grams of the chondrites Allegan and Farmington with HF and HNO$_3$. A diffractometer was used and silicon was the internal standard. The cell edge of Allegan chromite so determined is 8.34±0.01 Å and Farmington chromite gives 8.35±0.01 Å, both of which values are close to that of ideal chromite (8.38 Å; Deer et al., 1962), but slightly less, presumably because of substitution of Mg and Al.

**DISCUSSION**

Despite the small chemical variations among the chondrites and among the analyzed chromites, amounts of major oxides present in the chromites do appear to show a relation to the chemistry of the meteorites (Table 1). Chromite from the H-group chondrites tends to be high in Cr$_2$O$_3$ and Al$_2$O$_3$, whereas L- and LL-group chromites contain lower amounts of these oxides; and chromite in H-group chondrites tends to contain less TiO$_2$ than those from L- or LL-group chondrites. MnO appears to be less abundant in chromite from the L- and LL-group chondrites than in H-group chromite.

A most noteworthy feature is the variation of FeO and MgO in the chromites. FeO tends to increase, while MgO decreases in amount, in passing from H- to L- and LL-group chondrites. This is exactly the relation shown by the olivines and pyroxenes in these meteorites: FeO in the ferro-magnesian silicates increases from H to L to LL groups, and MgO decreases (Keil and Fredriksson, 1964). Because iron and magnesium trends are the same in the chromites and in the ferromagnesian silicates, it is suggested that, in the meteorites studied, chromite is in equilibrium with the ferromagnesian silicates, a situation that may be the result of (1) equilibration during contemporaneous crystallization of iron-magnesian silicates and the chromite or (2) equilibration during contemporaneous metamorphism of chromite and silicates.

Chromite from the Farmington chondrite does not, however, fit in with this relation of chromite composition to chondrite chemistry for Farmington is an L-group chondrite, the chromite of which is, in comparison to the current examples, high in MgO and Cr$_2$O$_3$, and low in FeO.
(Buseck and Keil, 1966). As methods similar to the ones described above were used in analysis of Farmington chromite, the discrepancy is not analytical. Rather it appears that Farmington may have undergone a different history than the chondrites dealt with in the present study, because Farmington chromite contains exsolved rutile and ilmenite lamellae. Chromite from the Dosso L-group chondrite, analyzed by Jérémie et al. (1964), likewise does not follow the trend of the chromites studied here; in this case the discrepancy may in part be analytical.

Work just completed (Bunch et al., 1967) with chromite in a large number of other “equilibrated” chondrites has verified the relation of chromite composition to composition of ferromagnesian silicates, and has, in addition, revealed that, within the three major ordinary chondrite groups, chromite composition is related to the petrographic subgroup (Van Schmus and Wood, 1967) of the meteorite.

Acknowledgments

We are grateful to Prof. Paul Ramdohr for critical manuscript review. Mr. Jozef Erlichman and Mr. John Vongrey assisted with the microprobe measurements. Analyzed terrestrial chromites, used to evaluate the standard chromite and determine empirical fluorescence corrections for Cr and Ti, were very kindly provided by Dr. E. D. Jackson, U.S. Geological Survey, Menlo Park, California; we are also grateful to Dr. Jackson for discussions on recalculation of the chromite analyses. Two of us (K. G. S. and T. E. B.) are supported by National Academy of Sciences—National Research Council Postdoctoral Research Associateships.

References


CHROMITE FROM CHONDrites


Manuscript received, December 15, 1966; accepted for publication, June 6, 1967.