CHAPTER FIVE

Characteristics of Chromite mineralisation
CHAPTER V

CHARACTERISTICS OF CHROMITE MINERALISATION

Introduction

The chapter deals with the mode of occurrence, structures, and textures, ore petrography, X-ray diffraction analyses, Mossbauer spectroscopic analyses, scanning electron microscopy and electron probe microanalyses of chromite ore minerals. On the basis of mode of occurrence, mineralogy and chemistry the chromites have been classified.

Chromite is the only ore mineral of chromium and most of it, throughout the world, is mined from rocks of mafic and ultramafic composition. Traditionally the chromite deposits are subdivided into two types. Stratiform ores which are associated with mafic-ultramafic layered intrusions, majority of which are of Precambrian age and have an intracratonic setting. The other category of deposits which are associated with the ultramafic-mafic complexes of the orogenic belts are generally referred to as 'alpine-type', a term employed after the rocks in which they occur. Although the deposits, like the rocks in which they lie, may be
called 'alpine', the term is superseded by the term 'podiform', which signifies the inherent form of these deposits. The term podiform has, therefore, priority over the term alpine, and will be followed in the present work. The term podiform was used as a noncommittal term by Wells (in Thayer, 1964) and others because of the similarity in form of many deposits to seed pods in plants. The term podiform may be defined (Thayer, 1964) as a fundamentally lenticular concentration of chromite ranging from massive to disseminated that occur in peridotite-gabbro complexes of the alpine-type (Thayer, 1964; 69). They are mainly Phanerozoic in age, have an irregular geometry, limited geographical extent and are associated with ophiolites.

The Chromite Deposits

The chromite deposits are found within the ultramafic rocks of the Indus Ophiolite Belt, in the Ladakh district of Jammu and Kashmir. The ophiolite belt extents in a NW-SE direction from Dras in the west to Hanle in the east, over a distance of 450 km. It has a maximum width of about 30 km. The chromite mineralisation along this belt is known from Dras, Norimis and Hanle (Prasad and Singh, 1981). The ultramafites occur as disconnected bodies tectonically emplaced within the rocks of Dras Volcanic Group (Scarle, 1981).
During the course of present investigation the chromite deposits around Dras and Tasgham have been investigated. The ultramafic rocks around Dras occur in the form of an elongated body that extends in WNW-SE direction over a strike length of about 5-6 kms. In the west the ultramafic rocks are exposed about 3 km NNW of Dras and continue in the east, west of helipad across Sandhu nala. They exhibit a maximum width of about 1.8 km.

The body is best exposed about 1.5 km north of Dras village and is known as Orange Hill (Plate V, Photo 1). The ultramafic rocks, as described earlier, are predominantly constituted of pyroxene peridotites and dunites. The former are mainly represented by harzburgites with subordinate wehrlites. The harzburgites are gradational into dunites with progressive disappearance of orthopyroxene. The peridotites and dunites occur within sheared and mylonitised serpentinite. The mylonitisation is generally seen along the sole of thrust sheet.

The chromite mineralisation occurs as pods (Plate XVIII, Photo 2) lenses, bands and streaks (Plate XIX, Photo 1) within dunites and the harzburgites. However, the concentration is more in the dunites than in the harzburgites. The chromite pods and lenses vary
from a maximum width of 8 m in length and half a meter in width to about 25 cm in length and 5 cm in width (Plate XIX, Photo 2). The pods and lenses generally trend N 20°E - S 20°W with steep dips, and in places are even vertical. The ore in the pods is generally massive with very little interstitial silicate. The chromite also occurs in the form of banded ores. The chromite bands are in the form of tabular lenses that taper along the length of the lense and also along the width. The bands are seen alternating with dunitic matrix (Plate XX, Photo 1). The bands extend in length from about 4 to 5 meters to 10 cms. Individual chromite band is made up of grains of chromite that are disseminated in a dunitic matrix. The proportion of chromite to silicate in different bands varies considerably. There are chromite bands in which the ore to silicate ratio is very high which makes the bands to look almost massive. While in other cases, the ore to silicate ratio is very low, thus making the chromite look as disseminations in silicate. The chromite bands may have sharply defined contacts with the enclosing dunite or they may have gradational contact. At places, one contact of the band is sharp but the other contact is gradational.

In certain cases massive chromite occurs in the form of elongated lenticles. The lenticle is made
up of massive chromite with very little silicate. The longest diameter of the lenticle is much longer as compared to the width and thickness. Such ore-forms are referred to as pencil ores. In a section all these forms are gradational into one another and at places it becomes difficult to categorise a particular ore-form into one type or other.

Ore Petrography

Under ore petrography are included structures and textures exhibited by the ores in hand specimen. The minerology of the ores in microsection and polished section and the micromorphology of chromites as observed under scanning electron microscope.

Structures

The term, 'structure' is here used to include the forms and shapes of ore minerals and their aggregates, which can be studied and recognised with unaided eye in hand specimens. Some of the important structures observed include podiform structure, banded and disseminated structure, pull-apart structure, modular structure, chromite net structure occluded silicate structures, compact and massive ores with no silicates, streaks and vein-like stringers of chromite.
Podiform Structure

This is the most common structure exhibited by the chromites. The structure essentially resembles a seed pod, however, a variety of forms and shapes may be recognised which may be included under this structural type. The pods occur as sack-like masses, as tabular lenticular bodies, pencil-shaped bodies laterally impersistent, planar and linear segregations involving chromite and serpentised olivine that gives rise to schlieren structures.

The pods are generally made up of coarse grained chromite. The crystals are subhedral, the grain size of chromite varies between 2 and 4 mm and at places even more. The pods have sharply defined contacts with enclosing dunite. The pods vary in length from a couple of cm to more than 15 cm, and in thickness from 3 to 5 cm. The pods may occur singly or they may occur in clusters (Plate XX, Photo 2). A cluster of pods may exhibit a variety of shapes, from typical pods to irregular structure-type. All the variations in shape of the pods have been included by Thayer (1964) under podiform chromites. Some of the pods are very long compared to their thickness and in such cases they are pencil-like in shape. In such pods the central portion of the pod is made up of massive chromite with almost no interstitial silicates, while
the terminal portions of the pods on either sides exhibit higher proportion of silicate and the pod pinches out in the dunite. In the central portion the chromite crystals are more than 2 mm in size and are compactly segregated. The size of crystals diminishes to 0.2 mm along either extremities of the pod.

Banded and Disseminated Structure

The term band is used in preference to layer because the latter term has a genetic connotation. The banded structure is made up of alternating dark and light coloured bands. The dark coloured bands are of chrome-spinels which are seen alternating with light coloured bands of olivine.

The bands are found to occur in repetitive manner in a given hand specimen. The bands occur as tabular sheets which pinch out along their length and thus are lenticular in shape. The bands vary in thickness from a couple of mm to more than 3 cm. Individual band is made up of disseminated chrome spinels. The crystals of chromite are subhedral vary in size from less than a mm to about 2 mm, in diameter. The bands generally exhibit sharply defined contacts. At places a group of bands may have wedges of dunite-rich material. In some specimens a number of thin chromite-rich
and olivine-rich layers constitute a thick megaband (Plate XXI, Photo 1). Within such megabands the individual micro-bands may exhibit gradational contacts. The megabands in places are seen to bifurcate as a result of wedge of dunite coming in between them.

**Pull-apart Structure**

The structure is generally exhibited by chromite ores from massive pods. In this case the stretching or elongation of solid chromite, results in the development of transverse cracks in chromite perpendicular to the direction of elongation (Plate XXI, Photo 2). These fractures are filled by silicate minerals. At places, the massive portions of the banded ore also display this structure.

**Nodular Structure**

The nodules and large crystals of chromite have the same internal structure and hence Thayer (1969) prefers to give the term nodule for both. The same terminology is followed here. The nodules consists of aggregates of small crystals of chromite in a dunite matrix (Plate XXII, Photo 1). At places larger crystals of chromite more than 3 mm in diameter are also found in dunite matrix. The central portions of nodules generally consist of chromite crystals along with silicate
minerals. While the portions surrounding the core are generally devoid of silicates.

**Chromite Net Structure**

It is generally exhibited by chrome spinels from banded ores. The bands rich in olivine display rounded and at places elongated grains or grain aggregates of olivine surrounded by chrome spinels which are interstitial to olivine, so that chromite occurs as a network between olivine grains.

**Massive Ores**

Massive ores are generally seen in ooidiform structures and rarely in banded structures, wherein the central portion of band may show massive ores. They are hard, compact and massive with very little (Plate XXII, Photo 2) to almost no interstitial silicate. The grain size of chrome spinels is more than 3 mm. In general majority of crystals in the ore are subhedral. In many samples the chromite grains are polygonal closely packed with grain boundaries meeting in triple points at 120°.

**Occluded Silicate Structure**

The structure is exhibited by massive ores which contain little silicates in them (Plate XXII, Photo 2).
However, it is also exhibited by banded ores. In this case olivine or serpentine either singly or as an aggregate of grains is found enclosed within chromite, forming spherical or rounded elliptical islands of silicates within chromite.

**Minerology of Chromites**

Minerology of chromites has been investigated both in transmitted light and incident light. In microsections the chromites from massive ores are typically reddish brown in colour (Plate XXIII, Photo 2). The grains are generally subhedral to anhedral and they have very little interstitial silicates which are represented by chlorite and serpentinised olivines. The grains are generally stretched and elongated and are traversed by fractures perpendicular to the direction of elongation. The fractures are filled by silicates. Along the fractures and grain boundaries the chromite grains which are otherwise reddish brown colour show development of distinct black borders. In polished section, in incident light, the chromite is grayish white in colour. The reflectivity of chromite is in general moderate. It varies between 12 to 18 per cent for green light in air, with reference to pyrite standard with reflectivity of 54 per cent. Between crossed nicols, it is faintly anisotropic. In oil the chromite shows reddish brown internal reflection.
The borders of chromite grains, however, have higher reflectivity as compared to the core of the grains in general.

Such a high reflecting rim around chromite was called 'ferrit-chromit' by Spangenberg (1943), who described it for the first time. This rim may be with or without an outer rim of magnetite. The boundary between chromite and ferrit-chromit is generally sharp as in the ferrit-chromit-magnetite boundary. Since the description of 'ferrit-chromit' by Spangenberg (1943), many investigators (Den Tex 1955, Paragas and Ottman, 1966; Beeson and Jackson, 1969; Bliss and MacLean, 1975; Ulmer, 1974; Hoffman and Walker, 1978) have studied the high reflecting borders of chromite. They have all arrived at similar conclusion that the high reflecting borders are 'ferrit-chromits'.

Although ferrit-chromit has been well defined physically, it has been poorly defined compositionally. In the literature, it is found that many workers have labelled any altered chromite as ferrit-chromit, regardless of composition, resulting in a variety of compositions (Onyeagocha, 1974; Loferski and Lipin, 1983). In general, ferrit-chromit is depleted in Mg and Al and enriched in Fe with respect to unaltered chromite grain composition (Lipin, 1984).
In the case of chromites from Ladakh, all the chromite samples studied do not show 'ferrit-chromit' development and they do not show development of magnetite either. Therefore, those chromite grains which show black borders and exhibit a depletion in Mg and Al and enrichment in Fe along the margin compared to the core, have been referred to as ferrit-chromit, following Lipin (1984). Ferrit-chromit therefore, have been encountered in chromites from only one sample (172). As shown later in the chemistry of chromites, the chrome spinels from this sample show margins of the grain depleted in Al and Mg and enriched in Fe compared to the composition of the core. Onyeagocha (1974) attributes this behaviour to the following reaction.

\[
\text{Chromite} + \text{enstatite} + \text{olivine} + \text{fluid}_1 = \text{Ferrit chromit} + \text{Chlorite} + \text{Olivine} + \text{fluid}_2
\]

This reaction takes place above the stability field of serpentine. The result of such a reaction requires that chromite looses Al and Mg and these would be used in the formation of chlorite. In the chromite under consideration the loss of Al and Mg is accompanied by a decline in Cr / Fe\(^{+3}\) from core to margin. This may be attributed to oxidation of Fe\(^{+2}\) to Fe\(^{+3}\). Similar change of chromite to ferrit-chromit is observed by
Bliss and MacLean (1975), Hoffman and Walker (1978) and Ulmer (1974).

There is little agreement among various workers about the process by which ferrit-chromit is formed. Bliss and MacLean (1975) suggested that chromite and serpentine related magnetite reacted to form ferrit-chromit. In the opinion of Hoffman and Walker (1978) ferrit-chromit represents an intermediate product formed by reaction of chromite with serpentinising fluid. Ulmer (1974) has suggested that ferrit-chromit has formed from serpentinising fluids by overgrowth on chromite. In the present study, however, it is difficult to ascribe ferrit-chromit formation to a particular process. The point of importance, however, is that all the above said processes involve serpentinisation.

Refractive Index of Chromites

Refractive index measurements were carried out on polished chromite sample, using a commercially available (SOPRA, FRANCE) spectroscopic ellipsometer, in the wavelength range of 0.4 to 0.65 μm. In this technique a beam of known polarisation is incident on the specimen and the change in the polarisation after reflection from the specimen is observed. The significant parameter refractive index is then calculated from the equation:
where $\Delta A$ is the relative change in the amplitudes of the reflected and incident beams, $\Delta \phi$ is the relative phase difference between the two, $r_p$ is the reflection coefficient of the light polarised in the plane of incidence and $r_s$ is the reflection coefficient of the light polarised in the plane perpendicular to the plane of incidence.

In the spectroscopic ellipsometer, a characteristic time dependence is induced on the incident beam by rotating one of the component viz., polariser or analyser and the intensity obtained at the detector is analysed for the refractive index. In the present work a Rotating Polariser Ellipsometer (R.P.E.) is used. If the rotation frequency of the polariser is $w$ then the intensity at the detector can be expressed as:

$$I(t) = I_o(1 + \cos 2wt + 2\sin wt)$$

The ellipsometric parameter and are:

$$\tan = \sqrt{1 - r^2} \tan \alpha$$
$$\cos = \frac{B}{\sqrt{1 - r^2}}$$

where $\alpha$ is the azimuthal angle of the analyser measured with reference to the plane of incidence.
The results of the refractive indices are presented in Fig. 5.1(a). It is seen from the figure that the refractive index of the chromite is in the range of 0.4 to 0.65. It is clear from the figure that the value of the refractive index in the wavelength range remains almost constant. The value of the refractive index has been found to be dependent on the composition of the sample and surface roughness. The latter induced by mechanical polishing, can affect the ellipsometric measurements and thus affect the refractive index. Ellipsometric parameters being very surface sensitive, any rough surface can yield a lower value of refractive index than the actual one.

**Textures of Chromites**

The chromites in microsections and polished sections exhibit a variety of textural types and interrelationship with associated silicates. Some of the important textures observed are pull-apart texture, micro-reticulate ring texture, chain texture, occluded silicate texture, nodular texture, disseminated texture and massive ores.

**Pull-apart Texture**

This is the most common texture exhibited by the chrome spinels. It is generally exhibited by
Fig. 5.1a: Plot of the RI of chromites from Ladakh Himalaya

Fig. 5.1c: X-Ray diffractogram of chromites from Ladakh Himalaya.
massive ores from podiform chromites and also by massive portions from banded ores. The texture is constituted of stretched and elongated grains of chrome spinels which exhibit a set of parallel cracks perpendicular to the direction of elongation (Plate XXIII, Photo 1). The fractures are filled with silicates such as olivine, serpentine and chlorite.

**Micro-reticulate Ring Texture**

The texture is commonly observed in banded ores. In this texture the chrome spinels form a net-like framework of grains within which olivines or other silicates are enclosed (Plate XXIII, Photo 2). At places rounded to irregular olivines and serpentine are surrounded by a ring of crystals of chrome spinels around them. Such a texture is called as ring texture. Isolated chromite crystals within the ring, can be observed at places.

**Chain Texture**

The texture is generally seen in the banded and disseminated ores wherein the chrome spinels are scattered in a dunite matrix. Euhedral to subhedral chromite grains are joined together to form continuous
chains (Plate XXIV, Photo 1) such a texture is best observed in dunites that exhibit a tabular equi-
granular texture.

Occluded Silicate Texture

The texture is seen both in the massive ores as well as the banded ores. It is made up of rounded or irregular grains of silicates that are enclosed within chrome spinels in a poikilitic manner (Plate XXIII, Photo 2).

Nodular Texture

This texture is exhibited by banded ores as well as by nodular aggregates of chrome spinels that occur in a silicate matrix. The texture consists of a rounded aggregate of anhedral grains of chrome spinels or even large anhedral grains (Thayer 1969) that occur in olivine or serpentine matrix (Plate XXIV, Photo 2). Such nodules may be fractured and granulated producing irregular grains of chromite.

Disseminated Texture

This texture is generally observed in banded ores especially in dunite-rich bands. Individual euhedral to subhedral crystals of chromite are seen scattered throughout the silicate matrix displaying
no particular orientation. In deformed and mylonitized
dunites the chrome spinels are fractured and granulated,
and are found to occur filling fractures within the
silicates.

Massive Ores

The chrome spinels from podiform ores generally
display massive form. The chrome spinels in massive
ores are generally anhedral and form a compact chromitite
with little or no interstitial silicates.

Micromorphology under Scanning Electron Microscope

The chromite micromorphology and the surface
features of the chromite crystals were investigated under
a scanning electron microscope, as it offers a resolution
power thousand times more than the conventional
petrological microscope along with a wider range of
magnification and greater depth of field.

The scanning was done under a Cambridge
Stereoscan-150 Electron Microscope at 25 KV accelerating
voltage and 10 pico-ampere current intensity. Each
sample was scanned for about an hour with magnification
varying from 20 to 20,000 times. The micromorphological
features were photographed on a panchromatic black and
white 35 mm. negative film.
The samples were selected from partly weathered harzburgites and dunites containing chrome spinels, so that the chromites were standing out a little above the surface of the enclosing silicates. The sample chips were acid treated to remove adhering silicates and cleaned. The chips of cleaned chromite were mounted on aluminium stubs and coated by gold / palladium alloy of 100 Å thickness.

Leblanc (1980) has carried out a comparative study of morphological features of chrome spinels from ophiolite peridotites and those from cumulates overlying mantle peridotites from ophiolite complexes and also stratiform cumulates from Bushveld complex. During the course of present investigations the micromorphologies of chrome spinels from Ladakh Himalaya were compared with the observations of Leblanc (1980). Additionally chromite samples from Sindhuvalli ultramafic rocks which are considered to be of stratiform type (Srikantappa et al., 1980, Naganna and Nijagunappa, 1983) were also scanned for comparison.

It was observed that many of the features exhibited by chromite from ophiolite peridotites (Leblanc, 1980) were observed in the chromites from peridotites of Indus Ophiolite Belt, in good agreement with Leblanc (1980).
Scanning electron micrographs of crystals of chrome spinel from banded ores exhibit subhedral form with rounded crystals edges (Plate XXV, Photo 1). Some of the crystals are subhedral ovoid in form. At higher magnification the faces of the chromite crystals show a rough jagged and pitted appearance. The pits are at places aligned in a particular direction forming an array of linear pits. The array of pits is generally controlled by the dislocation planes or cleavage planes. At places the pits join each other and coalesce to form furrows (Plate XXV, Photo 2). These may indicate movement direction along slip planes, or dislocation planes (Leblanc, 1980).

The chrome spinels from nodular chromites from peridotites were also scanned. In the scanning electron micrographs the chrome spinels from nodular ores exhibit a bunch of subhedral crystals with rounded edges (Plate XXVI, Photo 1) and convex looking crystal faces. The chrome spinels from massive podiform ores exhibit anhedral crystals with rounded edges. The surface of crystals are full of pits so that the surface has a appearance of a vermicular pattern (Plate XXVI, Photo 2). The silicates filling the pull-apart fractures in chromite are represented by serpentine which exhibit a typical step-like appearance (Plate XXVII, Photo 1).
The chlorite associated with net textured occluded ores under S.E.M. typically exhibits the micaceous and flaky habits of the mineral (Plate XXVII, Photo 2).

**Mossbauer Spectroscopic Analysis**

Theory of emission or absorption of gamma ray photons without loss of energy due to recoil of nucleus and without thermal broadening is known as Mossbauer effect. This technique can be used in characterisation of iron bearing compounds and in determining their magnetic properties. In an attempt to study the structural site distribution of Fe.

Two samples of chromite namely massive banded and banded chromites from Ladakh Himalaya were analysed. The chromites were crushed to 120 mesh size and were separated from the silicate gangue by hand picking under a binocular microscope. Subsequently the separated chromites were powdered to 200 mesh size and Mossbauer spectrum was recorded on a ECIL Mossbauer spectrometer. The spectrum was recorded at room temperature with 5 mc, 57 Co source dopped in rhodium matrix with a constant acceleration Mossbauer spectrometer. The spectra were computer fitted using MOSFIT programme of ICL 1904 S. The spectra are shown in Fig. 5.1(b). The values for isomershift and quadrupole splitting for the
chromites are presented in Table 5.1

The Mossbauer spectra (Fig. 5.1 b) of the chromite samples from Ladakh Himalaya clearly show one singlet with isomer shift (I.S.) of 0.525 mm/sec, and two doublets with isomer shifts of 1.65 mm/sec and 1.46 mm/sec, and quadrupole splitting of 1.19 mm/sec and 0.74 mm/sec, respectively.

The value of isomer shift of the singlet indicates that Fe is in Fe$^{+2}$ state. A slightly broad nature of resonance lines indicates the presence of Fe Cr$_2$O$_4$ - like phase in the sample. The hyperfine parameters of both the doublets show that Fe is in Fe$^{+2}$ state existing in FeAl$_2$O$_4$ - like structure. Such resolution of two sites is reported in the literature. However, it is to be noted that the values of isomer shift are on the boundary of Fe$^{+2}$ and Fe$^{+3}$. Therefore, it is concluded that some iron in Fe$^{+3}$ state may be present in the crystal structure. The presence of iron in Fe$^{+2}$ corresponds to the solid solution of FeCr$_2$O$_4$ and FeAl$_2$O$_4$ like phases in the ratio of 1 : 3.

X-ray Diffraction Analysis

X-ray diffraction is one of the most widely employed techniques used for the study of minerals. In this technique a beam of X-rays is directed on to
Table No. 5.1: Mössbauer parameters of chromite from Ladakh Himalaya

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Isomer Shift</th>
<th>Quadrupole splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>172</td>
<td>0.525</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>1.651</td>
<td>1.199</td>
</tr>
<tr>
<td></td>
<td>1.468</td>
<td>0.746</td>
</tr>
<tr>
<td>173</td>
<td>1.414</td>
<td>1.741</td>
</tr>
<tr>
<td></td>
<td>1.410</td>
<td>0.786</td>
</tr>
</tbody>
</table>
Fig. 5.1(b): Mossbauer spectrum of chromites from Ladakh Himalaya.
the specimen surface. The specimen mounted on a specimen holder is tilted at a fixed rate, so that X-rays are incident on the specimen surface at different angles. At certain angles these rays will be reflected back which are called Bragg's reflection. With the change in the angle of incidence, the angle of diffraction also varies. The reflections are recorded on the diffractogram. The angle of diffraction (2θ) corresponding to the reflection is noted and the 'd' value is calculated according to Bragg's equation:

\[ n\lambda = 2d \sin \theta \]

X-ray analysis of chromite samples were carried out by a Phillips PM 9920/05 X-ray diffractometer using CuKα radiation and Nickel filter. The samples were studied by powder diffraction method. The diffraction characteristics were recorded from 2θ to 40° 2θ using a linear scale of 10,000 cycles per second at a scanning speed of 1° per minute and a chart speed of 1° per cm, with a slit width of 0.2 mm. The diffractogram of representative sample is presented in Fig. 5.1 (c). It is seen from the figure that the sample shows a strong diffraction peak at 2.47 Å° with three additional peaks of moderate intensity at 1.59, 1.46 and 2.06 Å°. All these peaks match well with magnesiochromite. The cell
constant has been calculated making use of the following equation:

\[ \sin^2 \Theta = \lambda^2 \left( h^2 + k^2 + l^2 \right) / 4a^2 \]

where \( \Theta \) is angle of diffraction

\( h, k, l \) are the indices of the crystal face

\( \lambda \) is the wave length

The values of 'a' the cell constant vary between 8.23 and 8.26 Å in most of the samples studied. From the chemical analysis (Table No.3.8). It is seen that Mg > Fe\(^{+2}\) in most samples except sample No. 31 (Wehrlite). Therefore, the chrome spinels may be identified as magnesiochromites (Deer et al., 1965). In sample No.31 however, the chrome spinel is chromite (Deer et al., 1965) Part of Cr is substituted by both Al and Fe\(^{+3}\).

Chemistry of Chromites

Chromites from massive chromitites, those from pods in dunites, disseminated chromites from dunites, chromites from partially serpentinised dunites and disseminated chromites from wehrlites were analysed for their major element compositions with the help of electron probe microanalyser. In all seven representative samples of chromite bearing rocks were selected for study. From each rock at least 2 grains of chromite
were analysed. In order to determine variation in chemical composition within a grain, it was analysed from core to margin. The composition of the margin was determined at a point about 10\% inside from the margin of the grain. Similarly to know the variation from grain to grain more than two grains were analysed from each sample. In all 18 microchemical analysis including those of cores and margins are presented in Table No.3.8. Total iron was determined as FeO. Fe\(^{3+}\) and Fe\(^{2+}\) were calculated on the basis of spinel stoichiometry so that the ratio \(R^{3+} : R^{2+}\) is 2:1. The major element oxide weight percentages were recalculated to cations on the basis of spinel stoichiometry with 24 cations per 32 oxygen.

From the chemical data it is seen that majority of chromite grains show chemical zoning. Chromites from chromitites (173A, 173B) display distinct zoning. There is a slight increase in the \(\text{Cr}_2\text{O}_3\) from core to margin in 173A and a reverse behaviour of these oxides is observed in 173B. The chromites from chromitites in general are very rich in \(\text{Cr}_2\text{O}_3\), which varies between 57 to over 62 percent. The chromites from banded ores in DB4 also exhibit enrichment of \(\text{Cr}_2\text{O}_3\) and impoverishment along borders, however, in sample 172 reverse relationship is observed. In the case of disseminated ores from
fresh unaltered dunites (170) the cores are richer in Cr$_2$O$_3$ than the borders. The accessory chromites from wehrlite (30) also exhibit chemical zoning with border of chromite grains being richer in FeO and Al$_2$O$_3$ than the core. Cr$_2$O$_3$, however, does not show much variation from core to margin.

It is also observed from the table that the percentage of Cr$_2$O$_3$ in general decreases from massive chromitites (173A, 173B) to banded chromites (DB4) to disseminated chromites (190) to Wehrlites (30). It is maximum over 62 per cent in massive ores 173B and decreases to about 42 per cent in Wehrlites (30). An increase in Cr$_2$O$_3$ percentage is observed with increasing modal (173A, 173B) per cent chromite. The massive chromites and the banded chromites (DB4, 172) display typical podiform chromite composition in having more than 55 per cent Cr$_2$O$_3$, less than 15 per cent FeO and less than 0.3 per cent TiO$_2$ - a feature typical of podiform chromites from alpine peridotites (Dickey and Yoder, 1972). In all these ores Cr$_2$O$_3$ and Al$_2$O$_3$ show an inverse relationship while Cr$_2$O$_3$ does not show any significant correlation with FeO. The latter is almost constant within limits of 10.57 to 16.30 per cent. The TiO$_2$ content is in general low less than 0.3 per cent and it does not show any significant correlation with any of the major elements. (Thayer, 1964; Dickey 1975;
Greenbaum 1977). They also contain higher percentage of MgO over Al₂O₃, that is they are more magnesian. Thayer (1970) observed that in chromites containing more than 45 per cent Cr₂O₃ total iron rarely exceeds 16 per cent. Present chromite compositions are in good agreement with Thayer’s (1970) observations. The (Cr + Al) variation in chromites is small, whereas the Mg/ (Mg + Fe²⁺) ratio shows broader range in composition as compared to its restricted range in the co-existing silicates. It varies from 0.66 to 0.76. These chromites are characterised by a relatively constant Fe³⁺/ (Cr+Al+Fe³⁺) ratio ignoring the marginal zones. A positive correlation is observed between Cr⁺ / (Cr + Al) and Fe²⁺ / (Mg + Fe²⁺).

They are also characterised by an almost constant Fe/Mg which shows a range from 0.3 to 0.5, which according to Dickey (1975) is a characteristic feature of an individual deposit. The FeOₓ/MgO ratio is about 1 the range being 0.64 to 1.16. Similarly the ratio Cr/Al in these samples remains almost constant within limits. The maximum variation observed is from 2.98 to 3.8, which according to Dickey (1975) is the result of either bulk chemistry or temperature of crystallisation. Higher Cr/Al ratios are characteristic features of chromite derived from partial melting (Dickey 1975).
The Cr/(Cr + Al + Fe$^{3+}$) ratio does not show much variation. It ranges between 0.70 to 0.76 and it has an inverse relationship with Fe$^{3+}$(Cr + Al + Fe$^{3+}$) which in turn has an inverse relationship with Al / (Al + Cr + Fe$^{3+}$). The Mg / (Mg + Fe$^{2+}$) has an inverse relationship with Fe$^{2+}$(Fe$^{2+} + Mg$) ratio of chromites.

The chromites disseminated in dunites (170), those from partially serpentinised dunites (31) and those from wehrlites (30) typically show chemical characters that differ from the chromites discussed above. These latter chromites contain about 55 per cent Cr$_2$O$_3$. They exhibit a negative relationship between Cr$_2$O$_3$ and Al$_2$O$_3$ and an inverse relationship between Cr$_2$O$_3$ and FeO. Another characteristic feature of these chromites is that they contain higher percentage of Al$_2$O$_3$ over MgO, that is they are more aluminous as against those previously described which are more magnesian. The TiO$_2$ content in these samples is more than about 0.3 per cent, it varies between 0.28 to 0.45 per cent. Total iron in all these chromites is over 16 per cent, varying between 20.36 to 27.09 per cent. The Mg / (Mg + Fe$^{2+}$) ratio in these samples is comparatively lower and varies between 0.45 to 0.54. Fe$^{2+}$/ Mg is also distinctly higher varying from 0.82 to 1.2. The Cr/Al ratio varies between 1.37 and 2.59. Such low ratios are generally
shown by cumulus chromites (Dickey, 1975). The FeO$_t$/MgO ratio is about 2.5 in the range being 1.81 to 2.8. (Cr + Al) and Mg / (Mg + Fe$^{+2}$) do not show much variation. The (Cr + Al) varies between 14.4 to 15.5. Mg/(Mg + Fe$^{+2}$) ratio ranges from 0.45 to 0.54. A negative correlation is observed between Cr/(Cr + Al) and Fe$^{+2}$/ (Mg + Fe$^{+2}$). Similarly not much variation is observed in the Fe$^{+3}$/ (Cr + Al + Fe$^{+3}$) ratio which varies between 0.47 to 0.94.

In order to bring out the characteristic features of the chromites, the chemical data have been plotted in different variation diagrams. In the (Mg Fe) O Al$_2$O$_3$ - (Mg Fe) O Cr$_2$O$_3$ - FeO Fe$_2$O$_3$ triangular diagram (Fig. 5.2) of spinel compositional prism of Steven (1944), twelve chromites plots in the field of aluminian chromites, four plot in the field of chromian spinels, while two lie near the chromian spinel - ferrian spinel field boundary. In the Cr - Al - (Fe$^{+3}$ + Ti) ternary variation diagram (Fig. 5.3) majority of the Himalayan chromites plot in the field of alpine chromites, except for five plots which fall in the overlapping field of alpine and stratiform chromites.

In the 100 Mg / (Mg + Fe$^{+2}$) versus 100 Cr / (Cr + Al) face of the spinel prism (Irvine, 1967; Leblanc et al., 1980) most of the Himalayan chromites plot in the overlapping
Fig. 5.2: (MgFe)O·Al₂O₃ - (MgFe)O·Cr₂O₃ - FeO·Fe₂O₃ triangular diagram showing compositions of chromite from Ladakh Himalaya.

(after Stevens, 1944)
Fig. 5.3: Cr-Al-(Fe$^{3+}$+Ti) triangular plot for chromites from Ladakh Himalaya.
fields of chromites from alpine and stratiform complexes (Fig. 5.4a). However, the massive and banded ores are clustered together and are clearly separable from the disseminated chromites from dunites and accessory chromites from wehrlites.

In the 100 Mg / (Mg + Fe\(^{+2}\)) versus 100 Fe\(^{+3}\) / (Cr + Al + Fe\(^{+3}\)) diagram most of the chromites except three plot in the overlapping field of alpine and stratiform complexes (Fig. 5.4b). Three chromite analyses, however, distinctly plot in the field of alpine chromites. In this diagram too the plots show two distinct clusters separable from each other.

A plot of weight per cent FeO\(_t\) versus weight per cent Cr\(_2\)O\(_3\) is depicted in Fig. 5.5a. In this diagram the chromite analyses plot in the overlapping field of alpine and stratiform complexes. Two of the plots, are, however, located in the field of alpine chromites and 8 analyses plot in the field of stratiform chromites. In the TiO\(_2\) versus Al\(_2\)O\(_3\) variation diagram (Fig. 5.5b) most of the Himalayan chromites except four, plot in the fields of Antalya, Troodos and New Caledonian chromites, indicating their likeness to podiform chromites. Four plots, however, lie in the field of stratiform chromite. These latter chromites may be related to cumulate sequence of ophiolite complexes.
Fig. 5.4: Plot of $100\text{Mg} \;/ \; (\text{Mg} + \text{Fe}^{+2})$ vs. $100\text{Cr} \;/ \; (\text{Cr} + \text{Al})$ for chromites from Ladakh Himalaya.

(a)

(b)

Fig. 5.4: Plot of $100\text{Mg} \;/ \; (\text{Mg} + \text{Fe}^{+2})$ vs. $100\text{Fe}^{+3} \;/ \; (\text{Cr} + \text{Al} + \text{Fe}^{+3})$ for chromites from Ladakh Himalaya.
Fig. 5.5a: Plot of wt.% FeO$_1$ vs. Cr$_2$O$_3$ for chromites from Ladakh Himalaya.

Fig. 5.5b: Plot of wt.% TiO$_2$ vs. Al$_2$O$_3$ for chromites from Ladakh Himalaya.
The cation ratios have been plotted in the 100 Cr / (Cr + Al) versus 100 Mg / (Mg + Fe$^{2+}$) diagram (Fig. 5.6a) after Leblanc et al., (1980) with compositions of associated olivines. It is seen that majority of chrome spinels from massive and banded ores occupy the field of chromites from New Caledonia with Fo content of olivines of more than 95 per cent. The disseminated chromites from dunites, serpentinised dunites and wehrlites, lie in the field of chrome spinels from peridotites of New Caledonia and show a good agreement with the lower values of Fo contents of the associated olivines. The aluminous spinels from harzburgites also plot in the same field however, the associated olivines have lower Fo content.

The cation ratios have also been plotted in the 100 Cr / (Cr + Al) versus 100 Mg / (Mg + Fe$^{2+}$) diagram (Fig. 5.6b) showing the fields of chromites from different ophiolite and alpine complexes (Leblanc et al., 1980; Greenbaum, 1972; Juteau, 1975; Malpas and Strong, 1975). It is seen that in this diagram 10 analyses of chromites from Ladakh Himalaya, distinctly cluster together. They define a separate field and have a distinct identity. Out of the remaining 8 analyses, 5 plot in the overlapping field of chromites from Troodos, New Caledonia, Bay of Islands and Josephine
Fig. 5.6: Plot of $100\times{Cr}/(Cr+Al)$ vs. $100\times{Mg}/(Mg+Fe^{+2})$
(a) with compositions of associated olivine,
(b) showing fields of chromites for ophiolite and alpine complexes,
for the chrome spinels from Ladakh Himalaya.
peridotite, and the remaining 3 analyses occupy overlapping field of Antaliya and New Caledonia.

**Chrome Spinel as an Oxygen Fugacity Indicator**

It has been shown with the help of experimental and theoretical work (Irvine, 1965, 67; Ulmer, 1969; Hill and Roeder, 1974; Fisk and Bence, 1980) that a major factor governing the crystallisation of chromite is the prevailing oxygen fugacity apart from the Cr₂O₃ and Al₂O₃ content of the magma. The composition and stability of chromites therefore, is dependent upon the fO₂ of the system. At constant temperature, an increase in oxygen fugacity could lead to:

(i) abundant crystallisation of chromite thereby affecting the local distribution of trace elements such as chromium in the liquid

(ii) an increase in the value of Fe³⁺ / Fe²⁺ in the crystallising chromites, and

(iii) an increase in the magnesium content of the crystallising chrome spinel and the coexisting ferromagnesium silicate minerals.

Based on experimental and theoretical work, (Irvine, 1965; 67; Ulmer, 1969; Hill and Roeder, 1974; Snethlage and Von Gruenewaldt, 1977; Fisk and Bence, 1980)
analyses of chromite - olivine - orthopyroxene, which
is a oxygen fugacity sensitive assemblage, can be used
to calculate $f_{O_2}$ on the basis of principle outlined by
Irvine (1965). Thus, following Irvine (1965), $f_{O_2}$
can be related to the composition of coexisting spinel-
olivine-orthopyroxene by the following reaction:

$$6\text{Fe}_2\text{SiO}_4 + O_2 = 2\text{Fe}_3\text{O}_4 + 6\text{FeSiO}_3,$$ 
therefore

$$f_{O_2} = \left(\frac{a_{\text{mt}}^{\text{sp}}}{a_{\text{ps}}^{\text{opx}}}\right)^6 / K_D \left(\frac{a_{\text{ps}}^{\text{ol}}}{a_{\text{ps}}^{\text{ps}}}\right)^6$$

As the reaction involves the iron-rich and
members and magnetite, the calculated fugacities should
not be considered as absolute values but are useful
solely to indicate relative variations. Since the
compositions of olivine, pyroxene and spinel may all
be related, $f_{O_2}$ may be determined on the spinel
composition alone, if other phases are present.

Thus Irvine (1965) has established $K_D$ to be
about $10^{-5.4}$ at $1250^\circ$C. He has contoured the spinel
composition prism (Stevens, 1944) with a set of surfaces
that represent the possible compositions for different
oxygen fugacities at constant pressure and temperature.

The compositions of the spinels from Ladakh
have been plotted on the $Fe^{3+}/(Fe^{3+} + Cr + Al)$ Vs $Mg/
(Mg + Fe^{2+})$ projection (Fig. 5.7) of spinel composition
Fig. 5.7: \( \frac{Fe^{3+}}{(Fe^{3+}+Cr+Al)} \) vs. \( \frac{Mg}{(Mg+Fe^{2+})} \) projection of Stevens' (1944) spinel composition prism contoured with theoretical constant oxygen fugacity isobars, for chrome spinels from Ladakh Himalaya.
prism (Stevens, 1964) contoured with theoretical constant oxygen fugacity isobars (Dick, 1977). The results are discussed in Chapter VI.

Classification of Chromites

The chromite occurrences from Ladakh occur as (i) massive lenticular bodies (ii) pod-shaped concentrations (iii) elongated pencil-like bodies (iv) nodules, (v) stringers which pinch and swell, and (vi) disseminations within dunites. This mode of occurrence is typical of alpine-type chromite deposits. Minerologically the chromites show properties that are also typical of podiform ores. Micromorphological features conform to features of podiform ores described from other parts of the world (Leblanc, 1980).

On the basis of chemistry also the chromites from Ladakh resemble very closely the compositions of podiform chromites. Thus it may be concluded that the major chromite occurrences from Ladakh can be categorised as podiform chromites from ophiolites. The chromites disseminated within dunites and wehrlites, however, can be categorised as cumulates resulting from the magmatic impregnation of dunites.