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GEOCHEMISTRY OF CHROMITES OF SUKINDA,
CUTTACK DISTRICT, ORISSA

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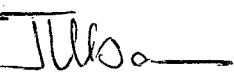
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PREFACE

The research work embodied in this dissertation has been carried out in the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi. The work is original and has not been submitted so far, in part or full, for any other Degree or Diploma of any University.


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CHAPTER 1

INTRODUCTION

The chromite deposits are associated with ultramafic and mafic igneous rocks. They occur in two different tectonic environments, giving rise to two different types of chromite deposits. The one which is associated with alpine type ultramafic bodies is called as the "podiform deposits" (Thayer, 1964). The other type is associated with large layered igneous complexes and is called as "stratiform deposits" (Jackson, 1961 and Thayer, 1964). In addition to their different host rock association podiform and stratiform deposits differ in their textures and geochemistry. The podiform deposits are characterised by nodular, cumulus and pull-apart textures which indicate that active tectonic forces were involved during their formation. The stratiform chromite associated with layered igneous intrusions appear to have been injected into comparatively stable tectonic environment under plutonic conditions. The stratiform chromite deposits are characterised by mesh pattern formed by minute chromite crystals packed around olivine or bronzite grains in the disseminated ore. The stratiform chromite deposits are nearly always associated with pyroxene, unlike the podiform chromite deposits which are generally associated with olivine (Thayer, 1969). They differ in their mode of occurrence as well. Stratiform chromites occur as extensive layers, traceable for several tens of kilometers and they have a regular stratigraphic position within the ultramafic part of the layered sequences. The

podiform deposits however, vary greatly in their form and size. They are generally lensoid, tabular and pod shaped. They are much less persistent as compared to the stratiform type. These deposits differ also in their chemical composition. The stratiform type generally have a regular variation in its chemistry laterally as well as vertically. The podiform chromites show no regular variation in their chemical composition.

Chromites are not only important because of their Cr content, but are also believed to be very good concentrator for platinum group elements (Waldrett & Cabri, 1976; Crocket et. al., 1976; Cousins & Ver~~pa~~^{iv}ok, 1976 and Razin & Khomenko, 1969). Although in India many important chromite deposits are known, no information is available on their platinum group elements concentration, except a passing mention of platinoids in Sukinda Chromites by Dasgupta (1959).

Chromite deposits of Sukinda were chosen for the present study. This is because of the fact that Sukinda chromites are the largest of the several Indian occurrences where chromite mining has been going on for the last several years particularly for export purposes. Further, these deposits have been studied in some detail for their geology and geochemistry by Banerjee (1961-72), Mitra (1958-76) and Chakraborty & Baidya (1978). In the present study, an attempt was made to look at the geochemistry of Sukinda chromite not only to understand their geochemical nature and therefore their

origin in the light of recent studies but also to determine the levels of concentration of platinum group elements. On the basis of available chemical data it is suggested that chromites of Sukinda are of alpine type origin, although it is not very clear whether Sukinda ultramafic complex is an ophiolite complex. Emission spectrography and atomic absorption spectrophotometric studies of the pure chromite samples indicated that the level of platinum group elements concentration must be lower than 1 ppm. A more careful and detailed study needs to be carried out to determine if platinum group elements are present in any economic concentration in the chromite deposits of Sukinda.

CHAPTER 2

PREVIOUS STUDIES ON CHROMITE ORE DEPOSITS

Chromite (FeCr_2O_4) is the only ore mineral of chromium, which occurs in abundance. Crocoite, (PbCrO_4), another ore mineral containing chromium, is far too rare as an ore mineral. Chromite occurs as an accessory mineral or as differentiated, massive ore bodies in many ultramafic and mafic igneous rocks. It is a member of spinel group of minerals. These minerals occur as simple octahedra, sometimes combined with rhombdodecahedra or trapezohedra. Their structure is based on cubic close packing of oxygen atoms, with two kinds of interstices:

- (i) Octahedral - surrounded by six oxygen atoms and
- (ii) Tetrahedral - surrounded by four oxygen atoms.

The general formula for the spinel group of mineral is AB_2O_4
($\text{IV}_A \text{VI}_B \text{IV}_O$).

Where A represents divalent cation like $-\text{Mg}^{2+}$,

Fe^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} .

B represents trivalent cation like $-\text{Al}^{3+}$,

Fe^{3+} , Cr^{3+} , Mn^{3+} .

Pure chromite has the chemical formula (FeCr_2O_4).

Chromium is a very useful and important metal. The outstanding use of chromium is in the production of alloys, especially those of iron, nickel and cobalt. It possesses the property of imparting to iron and steel a high degree of hardness and tenacity.

So in the recent years, it has become one of the most important industrial mineral. The iron and chromium alloy (Ferrochrome) is commonly used, for this purpose. The low grade chromite is used very extensively as a refractory material for furnace linings. Other salts, artificially prepared, are used as pigments, and in various industries as chromium-plating, dyeing, tanning, photography etc.

Chromite deposits are classified into two major categories based on their mode of occurrence and associations:

1. Podiform type: These are associated with alpine type ultramafic bodies.
2. Stratiform type: These are associated with the layered igneous complexes.

The podiform chromite deposits: The term podiform deposit was first introduced by Thayer, to describe the class of deposits within peridotite of the ophiolite assemblage (Thayer, 1964). They occur as autoliths in the tectonite peridotite. According to Dickey (1975), their distribution is not predictable except for a vague tendency to lie near the transition zone below the cumulates. Typically these deposits are surrounded by dunite halos beyond which the country rock is harzburgite (Olivine + Orthopyroxene) or less commonly dunite itself. Most of these deposits are tabular lenses or irregular pencils or combinations of both these basic forms. The ore body varies irregularly from place to place within individual deposits and some times the shapes and forms even defy description. Well-banded schlieren plates of disseminated chromite is very common in the

tabular deposits. Some authors call the pencil-form deposits as injection pipes. There appears to be no relationship between the form of the ore body and its grade. Massive chromite ores have generally negligible amount of silicate minerals whereas in the disseminated ore the silicate minerals dominate over the chromite. Generally the disseminated ore grades into normal peridotite with chromite schlieren. The most common matrix minerals in the podiform chromites, are olivine and serpentine after olivine. According to Dickey, the surrounding country rocks are not as varied in silicate matrices as the podiform chromites are (Dickey, 1975). Thayer (1946 & 69) has reported extraordinary podiform chromites in Cuba that have a troctolite matrix, and in another unusual deposit in Celebration Mine, Oregon, the matrix consists of clinopyroxene. In Dubostica, Yugoslavia, Pamic found podiform chromites with amphibole matrix (Pamic, 1970). According to Thayer (1969), the podiform chromites can be readily distinguished from stratiform chromites, by the presence of nodular texture. Further he reported that all the nodular ore are not massive, but some are nodular concentration of loose chromite grains, whereas some are orbicular with cores or concentric zones of chromite and silicates (usually olivine and serpentine after olivine). The nodules seldom exceed a diameter of three centimeters, regardless of the overall chromite concentration in the rock. Dickey (1975) observed no major changes in Mg, Al, Cr or Fe concentration from the core to the edge of the chromite nodules, except for rims of Fe-rich chromite that form in

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serpentinized specimens. According to Thayer (1964), the podiform deposits show banding or layering with olivine in all proportions and lineation is as common as layering and in places may be more important and also causes banding in chromite ores. The chromite occurring in the pencil-shaped deposits are dominated by lineation as compared to layering. Most of the chromite grains. In both massive and disseminated ores, of podiform deposits are anhedral, but the accessory chromite in peridotite are sometimes euhedral. The massive ore having irregular grain boundaries with interlocking grains vary often in the grain size. In podiform chromites, sharply defined layers of coarse massive chromite may alternate with barren dunite or, lean, disseminated ore. The tabular or lineate schlieren ore bodies are at most about 0.8 Km. long. The lenses or pods of all shapes are measured in tens or hundreds of meters and may range to small irregular blobs. The boundaries of these deposits vary in character from place to place. It may be well defined or diffused, most of them are marked by small irregularities, fraying out of high-grade into low-grade ore and some have satellitic stringers in the wall rocks. The contacts are generally better defined along the sides or edges than the ends which may be rounded or terminated abruptly in different deposits.

Nature of rocks associated with podiform chromite deposits:

The podiform chromite deposits are associated with alpine type intrusions which are believed to be portions of ophiolite complexes, emplaced in the solid state during subduction of lithospheric

plates. These ophiolites themselves are interpreted as portions of the oceanic crust and upper mantle. They are characterized by a basal zone of metamorphic textured peridotite overlain by a sequence of cumulates ranging from peridotite to gabbro, a sequence of pillow lavas and associated feeder dikes, and a capping of deep-sea sediment (Naldrett & Cabri, 1976). The bulk composition of the intrusion is peridotite. The chromite ore deposits are associated with dunite, peridotite and peridotite-gabbro complex. Generally the chromite ore bodies occur in groups in the dunitic parts of peridotite masses or along the shear zones. According to Thayer (1967), the ultramafites and gabbro together constitute more than 90 per cent of the alpine type of bodies. Further, the ultramafites for most part are dunites and olivine-rich peridotites or serpentized equivalents, whereas the pyroxenites generally constitute less than 5 per cent of the total. The alpine type bodies are characterized by irregularities in forms, internal structures, and distribution of rocks which is generally erratic. The rocks show no change in composition towards the contacts except for higher degree of serpentization in peridotites. The gabbroic rocks are fine grained and massive near the contacts. The noritic border facies are conspicuously absent. The alpine-type peridotites never show any contact metamorphic effects on the surrounding rocks or even inclusions, which suggest cold intrusion. According to Leech (1953) and Smith (1958) the alpine type bodies have very sharply defined layerings, but are much less persistent than the stratiform complexes.

In the average alpine-type peridotites, Olivine predominates over pyroxenes in the ratio of about 4:1 (Leech, 1953) and the only accessory mineral is chromite. According to Hess (1955), the MgO:FeO ratio in the alpine type bodies is higher than the stratiform complexes, and the orthopyroxene contains much less CaO. The alpine peridotites may grade into gabbro or norite through either of the two intermediate facies, troctolite and olivine-gabbro or pyroxenites (Thayer, 1960). The texture generally is gneissic and contrasts markedly with the settled textures of the truly stratiform rocks. Dunite commonly exhibits cataclastic texture (Turner, 1947). The plagioclase in many alpine-type gabbroic rocks typically has mutual boundaries against the mafic minerals and their tabular form is not well developed. The grain size may range from very fine grained to coarsely pegmatitic with 10 to 15 cm. long crystals of pyroxene. Thayer (1970), based on the late magmatic history of peridotite, gabbro and peridotite-gabbro complex, classified the ultramafic complexes into three types, the authigenic, allogenic and polygenic. The rocks which have moved away from the original sites of differentiation and crystallisation as a relict crystalline aggregates are allogenic. The alpine peridotite gabbro complexes which contain podiform chromite are the best examples for this class. Many geologists believe that these peridotites originated in the mantle and their metamorphic textures and structural features are related to mechanism of ocean-floor spreading. Some petrologists suggest emplacement of alpine gabbro peridotite complexes partly as fluid

magma and partly as crystal mush (Moore, 1969 & Smith, 1958).

As to the mode of origin of the alpine-type ultramafites, the following are the views expressed: The alpine-type ultramafites are altered upper mantle rocks, exposed at the surface by an uplift of oceanic crust (Hess, 1960; Puerto Rico, Serpentine); fractional crystallisation from a basic liquid (Challis, 1965; the New Zealand, ultramafites); slices of the upper mantle, brought by diapiric rise (Green, 1964; Lizard area, Cornwall); or originally layered intrusion that had been deformed and metamorphosed during an orogeny (Bowe et al., 1964; Ultramafic masses in the Lewisian of Scotland).

The Stratiform type of Chromite Deposits:

The term "stratiform chromite" was given by Jackson (1961) and Thayer (1964) for the chromite deposits, occurring in large layered ultramafic and mafic intrusions as the Stillwater complex in Montana, and Bushveld complex in South Africa. The great layered intrusions and their constituent layered chromitites, all appear to have been injected into comparatively stable tectonic environment. Except for the massive ore, where the grains coalesce, the stratiform chromites otherwise forms minute euhedral crystals everywhere. In the disseminated ores the chromites crystals are packed around olivine or bronzite grains, giving rise to mesh pattern, which is the characteristic texture of stratiform deposits. Pseudomorphic bronzite, after olivine, is present and the original pattern is preserved. The massive ore is characterised by even grains, euhedral

and unbroken crystals and usually 10 to 20 per cent of interstitial gangue. In individual layer or sequences of chromite layers the most massive parts commonly are located at the stratigraphic base of the layer or group of layers and the higher parts are characterized by the presence of disseminated ores. Unlike the podiform chromites, the stratiform chromite deposits are almost always associated with pyroxenes. Kuschke (1940) reported that in Bushveld complex, much of the chromite actually occurs in bronzitite. The chromites and the silicate layers are very persistent, may be traced for thousands of meters, and they adhere rigorously to certain position in the ultramafic sequence. The chromite ores occur in relatively thin layers which are concentrated with chromites, and these layers according to Irvine (1967), are due to gravitational accumulation of early formed crystals. The chromites may be precipitated over a considerable part of the crystallisation history and they show compositional variation resulting from fractional crystallization.

Nature of the associated rocks with stratiform chromite deposits:

Wilson (1956) defined layered intrusions as plutonic bodies with regular, more or less saucer or funnel shaped masses which have well defined floors and were not removed by erosion. They are characteristically layered and their compositions ranging from peridotite at the base to gabbro or granite at the top (Hall, 1932, Peoples, 1933). They have chilled margins which indicate the

composition of the original magma. These chilled margins are surrounded by a zone of high temperature metamorphic rocks (Howland, 1954). The layering is due to in situ differentiation. The "mean" composition of any large individual layered intrusion is gabbroic, although the chromites are generally associated with ultramafic layers. The containing stratiform masses as a whole are mafic and not ultramafic. The variation in composition is very systematic and in places they show cyclic repetition. The ultramafic zone in the stillwater complex is divided into a lower peridotite member and an upper bronzitite member. According to Jackson (1961&63), the peridotite member may be subdivided into 15 "cyclic units" which are characterized by layers of poikilitic harzburgite, granular harzburgite and bronzitite arranged in that succession. The disseminated chromite ore in the poikilitic harzburgite occur in layered concentrations in 13 of the cyclic units and the chromite concentrations commonly have the same position in each cyclic unit. Jackson (1960) reported that the ultramafic zone in the stillwater complex has 65 per cent pyroxene, 25 per cent olivine and 10 per cent plagioclase, whereas the ultramafic part of the Bushveld complex contains even less olivine (Cameron and Emerson, 1959). According to Cameron (1963), in the Bushveld complex, the orthopyroxenite is the principal rock type associated with the lower chromite seams, the anorthosite and anorthositic norite predominate near the upper ones, however, all three of these rock types occur in alternate layers through most of the sections, and they are locally accompanied by minor amounts of

peridotite, troctolite and norite. Thus in the layered complexes the chromite deposits are sometimes associated with anorthositic rocks; in addition to the ultramafic rocks. According to the classification by Thayer (1970), the layered ultramafic rocks come under the authigenic type. The ore deposits are concentration of phases formed by simultaneous crystallization and settling of crystals or liquids from fluid magma. Concentration of sulphide minerals seems less consistent stratigraphically than oxide minerals, but they follow a differentiation trend from nickel and iron rich at the bottom, to iron and copper rich at the top of the layered body (Liebenberg, 1960).

GEOCHEMISTRY OF CHROMITES

The chromian spinel is an early magmatic mineral in most of its occurrences and where it is late, it is supposedly an "early crystallised mineral" as its typical host rocks include the dunites, peridotites and orthopyroxenites which are characteristically early magmatic differentiates. The chrome spinels may change their composition, if they are not completely isolated from the rest of the magma. They may undergo reaction because of its peritectic relationship with the melt. Thus, according to Irvine (1967), the compositional variation shown by spinel solid solution depends on the nature of peritectic relation, the stage and the way it is imposed, between the chromite and the existing melt or magma. According to Loney et. al. (1971) and Irvine (1965 & 67) the bulk composition of the magma and coexisting silicate phase as well as conditions of formation control

the spinel composition. However, Malpas and Strong (1975) found that spinels from the Gander River dunites are different from those of the Bay of Islands cumulus dunites, although there is similarity in bulk composition of the magma and coexisting phases. Likewise, they noted that despite significant differences in forsterite content of olivine from the harzburgite (F091-94) and dunite (F085-87) of the Bay of Islands, there is no correlative difference in the $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratio in the spinels from these rocks. So it appears that differing pressure-temperature conditions of formation must be the main controlling factors for the spinel compositional differences. The difference in chemical composition of chrome ore may be due to the differences in the partial pressure of oxygen during the crystallization of magma. When crystallisation takes place under low $p\text{O}_2$, the oxidation of divalent to trivalent iron would be suppressed. The entry of ferric iron into the chromite lattice would tend to be low under low $p\text{O}_2$, and high chrome spinel would crystallise (Osborn, 1959). According to Thayer (1946), the following hypothetical relationship between the chromite and the associated silicates exist:

The silica content of the magma theoretically should not have any significant effect on the composition of the chromite, as silicon does not substitute for any cations in the spinel structure and the silica combines readily to form silicates like Olivine and pyroxenes which are the associated phases with chromite. The absence of corundum and aluminian silicates from fresh peridotites suggests that under normal magmatic conditions even free quartz might not react

with chrome spinel and in places chromites remained apparently unaffected even though the original gangue has been completely silicified as is seen in the Sukinda Complex where the associated rocks have been silicified extensively and the chromite ores are unaffected. Generally the addition of silica to a mixture of chromite and olivine would result merely in the conversion of olivine to orthopyroxene. In a lime-rich environment, likewise, if sufficient silica is present to combine with all the lime to form anorthite, limited variation in silica will only change the enstatite-olivine ratio i.e., the enstatite will become more in excessive silica. If the pressure-temperature conditions favour the formation of chrome diopside, the variation of silica would obviously affect the composition of chromite. The composition of the chromite in a given peridotite mass might be expected to reflect the overall composition of the magma in several ways. First of all, the ratio of MgO to FeO in chromite is related to the composition of the olivine and enstatite, so that high iron chromite should accompany bronzitic saxonites and the high-magnesian chromite should be in forsteritic dunites. The ratio of FeO to Fe_2O_3 is a function of the state of oxidation of the iron in magma. Since the chromites constitute a very small proportion of the whole magma and as only negligible amounts of Fe_2O_3 are taken into olivine and enstatite, slight variation in the ferric iron content of the magma should be greatly magnified in the ratio of the iron oxides in the chromites. If chromites were

silicification
is post crystallization
of chromite

formed in a highly oxidized magnesian environment, it should be rich in Fe_2O_3 in the form of magnesium ferrite (MgFe_2O_4). However, as most chromites are consistently low in Fe_2O_3 , it is believed to have been formed in a less oxidizing environment. Thayer (1960 & 70) and Irvine (1967) have pointed out that chromites from alpine and stratiform complexes differ chemically in certain significant respects. The alpine chromite deposits generally show a wider range of Cr:Al and Mg:RO ratios and have a lower or more uniform iron oxidation ($\text{FeO}:\text{Fe}_2\text{O}_3$) ratio. According to Greenbaum (1977), the Cr:Al ratio from Troodos chromite ranges from 1.34 to 9.75. Dickey suggested that the chromites from podiform deposits are typically more magnesian than those from stratiform intrusions (Dickey, 1975). The $\text{Fe}^{2+}:\text{Mg}$ ratio for individual podiform deposits are almost constant, unlike the stratiform chromites where the ratio varies considerably. For example the chromites from stratiform Stillwater complex range in $\text{Fe}^{2+}:\text{Mg}$ ratio from 0.67 to 1.59, whereas the podiform chromites from Haggard and New Mine at Canyon Mountain vary between 0.40 and 0.45. The podiform chromites show bimodal character, concentrating into high-Cr and high-Al groups (Thayer, 1970). The exact reason for this bimodality has not been well understood. Many of the Cuban chromites have high-Al content and most of them are associated with troctolite rather than peridotite, thereby suggesting that the high Al-content reflects the high-Al content of troctolite. Dickey and Yoder noted strong influence of bulk Cr:Al ratio on

spinel composition, in a simple synthetic system (Dickey & Yoder, 1972). Dickey further reported that the stratiform chromites which follow a trend of Fe^{3+} variation, appear to bridge the gap in the podiform chromite data (Dickey, 1975). One of the explanations for the bimodal Cr:Al ratio may lie in the distinction between cumulus chromite (Low Cr:Al) and chromite that is residual after partial fusion (high Cr:Al ratio). These two types of chromite deposits can be easily distinguished on the basis of TiO_2 concentration. The podiform chromites generally contain 0.3 wt per cent TiO_2 , and the stratiform chromites generally contain more TiO_2 than the above value. The stratiform chromites have a relatively high content of ferrous iron (FeO:RO average about 50-55 mol per cent) and this is the principal cause of low Cr:Fe ratios, which averages about 1.5:1 (Thayer, 1960). Although in some stratiform chromites the Cr_2O_3 may exceed 50 wt per cent, in most of these deposits it ranges between 38 and 45 wt per cent. Although the Cr_2O_3 content in podiform deposits is generally high, it has a large spread between 16 and 65 wt per cent. The Cr:Fe ratio in unaltered podiform chromites range from 2:1 to 3.5:1, but in some cases it exceeds even 4:1. The mole per cent, FeO in RO ranges between 25 and 50 and it averages around 35 mol. per cent.

Crocket et. al. (1976) determined the concentration of Pt, Pd, Ir and Au in the Merensky Reef of the Bushveld Complex to study the relative importance of spinels, sulfides and platinoid minerals as carriers of platinum group elements. For this, they attempted to

compare the platinum group element concentration in the sulfide and spinel separates with their whole host rock. The highest values they got from a $\frac{1}{8}$ in (approximately one-eighth inch) band of chrome spinel with pronounced hydrous alteration of primary silicates. In Table (2-1) by them the Pt and Pd are the only platinum group elements which appear to have been strongly concentrated in spinel and composite grain (Table 2-1). If we do not include the sample 10 of Crocket et. al. (1976) then Pt is the only mineral which is showing comparatively strong concentration in spinels and composite grains as compared to the whole host rocks, otherwise the platinum group elements values obtained for spinel and composite grain samples differ little from the corresponding whole host rock values. According to Naldrett and Cabri (1976), from their studies of different types of ultramafic rock bodies and their associated ore deposits, the chromite concentrations and samples rich in disseminated chromite are generally higher in platinum group elements, particularly Pt and their data indicate that the $Pt/(Pt + Pd)$ ratio may be distinctly higher in chromite deposits than in the rocks as a whole in the alpine type ultramafic belts. Further they reported that as with alpine complexes, chromite-rich rocks and chromite concentrations and segregations from Alaskan-type complex are much richer in platinum group elements than the chromite poor rocks, and as with the rock themselves they may have a lower $Pt/(Pt + Pd)$ ratio than chromite deposits in alpine complexes. Regarding the stratiform complexes,

TABLE (2-1) (in ppm)

	<u>Pt</u>	<u>Pd</u>	<u>Pd^{1*}</u>	<u>Ir</u>	<u>Au</u>
Spinel & composite grain	9.5	33.1	1.9	0.081	1.27
Whole rock	4.2	3.2	0.98	0.075	0.82
Spinel/whole rock	2.3	9.2	1.9	1.1	1.6

*Pd¹ - Excluding values of sample 10 of Crocket et. al. (1976).

Table (2-1) - Average platinum group elements content of spinel and composite separate (50% chrome-spinel & 50% silicates) compared to the whole host rock values. After Crocket et. al. (1976).

the concentration of platinum group elements is highly variable. Cousins and Vermaak (1976), reported that the Pt/(Pt + Pd) ratio increases upwards in the Bushveld complex, South Africa. Table (2-2), given by Waldrett and Cabri (1976) for platinum group elements concentration in the alpine complexes, gives us an idea that the chrome spinels are very important carrier or concentrator of platinum group elements. The average value of platinum group elements concentration in the dunite and peridotite rocks is very low as compared to the chrome spinels associated with them in the Ural mountains.

It is not very clear whether this association of platinum group elements with chrome spinels is due to lattice substitution or to concentration in sulfide or other inclusions or presence of discrete platinoid within the spinels or if they occur along the grain boundaries. Crocket et. al. (1976) are of the opinion that the high Pt and Pd contents and the strong variability of Pt and Pd are probably due to occurrence of platinum group elements as discrete platinoid phases. Razin and Khomenko (1969) are of the opinion that it is due to ionic exchange because the chrome spinel has ionic bonding with a normal cation distribution in the structure and therefore it is possible that the chemically similar metals enter the chrome spinel lattice isomorphously. Table (2-3) indicates that the platinum group elements preferentially can replace Cr, V, Ti and Al. If we take into consideration the ionic radii and ionization potential of different elements (Table 2-4), the Cr^{3+} which have octahedral coordination and also V^{3+} are the most probable cations which can be replaced by the tetravalent platinum group elements by means of heterovalent replacement.

TABLE (2-2) (in ppb)

	<u>Ru</u>	<u>Rh</u>	<u>Pd</u>	<u>Os</u>	<u>Ir</u>	<u>Pt</u>
Dunite & Peridotite average, urals	0.62	1.99	18	5.1	5.7	73
Chromite separates & segregations: Massive chromite in dunite	750	61	3900	610	430	38000
Chromite disseminated in dunite			24	3.4	4.3	

Table (2-2)- Platinum group elements concentration in alpine complexes, after Waldrett & Cabri (1976).

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TABLE (2-3)

Elements	Mg	Al	Ti	V	Cr	Mn	Fe	Co	Ni	Ru	Rh	Pd	Os	Ir	Pt
Ionic or Atomic Radius \AA	1.60	1.428	1.477	1.401	1.453	1.70	1.63	1.62	1.60	1.410	1.364	1.38	1.45	1.35	1.37

TABLE (2-3) - IONIC OR ATOMIC RADIUS^o IN \AA OF DIFFERENT ELEMENTS BY RAZIN & KHOMENKO (1969) AFTER LEBEDOV (1967).

TABLE (2-4)

Cation	Ionic radii Å	Coordination No.	Ionization potential
Mg ²⁺	0.74	4	78.2
Al ³⁺	0.57	6	119.96
Ti ⁴⁺	0.64	6	99.8
V ³⁺	0.67	6	48.0
Cr ³⁺	0.64	6	(51)
Mn ²⁺	0.91	4	33.69
Fe ²⁺	0.80	6	30.64
Co ²⁺	0.78	4	33.49
Ni ²⁺	0.74	6	36.16
Mn ³⁺	0.70	4	(53)
Fe ³⁺	0.67	4	(56)
Ru ⁴⁺	0.62	6	(63)
Rh ³⁺	0.75	6	(46)
Rh ⁴⁺	0.65	6	(67)
Pd ²⁺	0.80	4	(33)
Pd ⁴⁺	0.64	6	(66)
Os ⁴⁺	0.65	6	(54)
Ir ³⁺		6	(39)
Ir ⁴⁺	0.65	6	(57)
Pt ²⁺	0.80	4	(29)
Pt ⁴⁺	0.64	6	(55)

Table (2-4) - Ionic Radii & Ionization potentials of different elements by Razin & Khomenko (1969), after Grigoryev (1966)*.

*NOTE: Estimated ionization potentials in parenthesis.

According to Razin et. al. (1965) only a part of the platinum metal form independent platinum minerals or platinoids, while a substantial fraction of their total content occur in the essential and accessory minerals of ultramafic rocks in the form of "nonmineral admixture". They introduced this term "nonmineral admixture" to collectively indicate occurrence of the platinum group elements in the form of adsorbed ions and of isomorphous and other admixture i.e., in other forms than independent platinoids. Razin and Khomenko suggested that the platinum-group metals occur in the early and late magmatic chrome spinels and therefore the parent magma was platinum-bearing (Razin and Khomenko, 1969). The chrome spinel was the early magmatic phase to act as a concentrator for the traces of platinum metals that are present in the magma. Razin et. al. (1965) reported that morphologically similar chrome-spinels separated from dunite, showing the same degree of epigenetic alterations but occur in different parts of the massif have different concentration of platinum group elements, the value is higher on the periphery and lower at the centre. So as a rule in any intrusion the peripheral magma solidifies first and the core part solidifies last. Thus the periphery represents higher temperature of crystallization and is comparatively better representative of the original magma than the core. It appears that the first crystallising chrome spinel took most of the platinum group elements present in the magma and therefore we get higher values at the margin.

In view of the fact that the chromites associated with ultramafic rocks of different origin constitute the best concentrator of platinum group elements, it was proposed to study the chromite deposits of Sukinda ultramafic complex (Banerjee, 1972) with particular reference to their geochemistry and platinum group elements concentration at least in a qualitative sense.

CHAPTER 3THE SUKINDA CHROMIFEROUS ULTRAMAFIC COMPLEX

The Sukinda ultramafic complex is located to the north-west of Sukinda Khas near the trijunction of Cuttack, Dhenkanal and Keonjhar districts of Orissa, between Saruabil and Kalarangi (21°0' - 21°5' North latitude and 85°45' - 85°50' longitude) as shown in the published Geological Map of Sukinda area attached (Fig. 3-1). It occupies a narrow, westerly sloping valley which is bounded to the north, east and south by steep hills towering upto 690 meters above the average valley level.

The rocks of Iron Ore Series in the Sukinda region were intruded by chromite bearing ultramafites during the Eastern Ghat Cycle Orogeny, between 2800 - 3000 m.y (Sarkar, 1968). According to Banerjee (1972) the ultramafites are about 1700 meters thick and consists of an early chrome-rich suite and a later chrome-poor suite. The earlier suite is now represented by talc-schists, serpentine and partly by completely silificied talc-tremolite rocks with tabular to lenticular chromite deposits. The later suite was emplaced along the central part of the chrome-rich ultramafites. These are coarse, pale apple-green orthopyroxene, which are also marginally altered into a talc-tremolite-serpentine aggregate. The complex has been folded into a westerly to south-westerly plunging, asymmetric, canoe-shaped syncline.

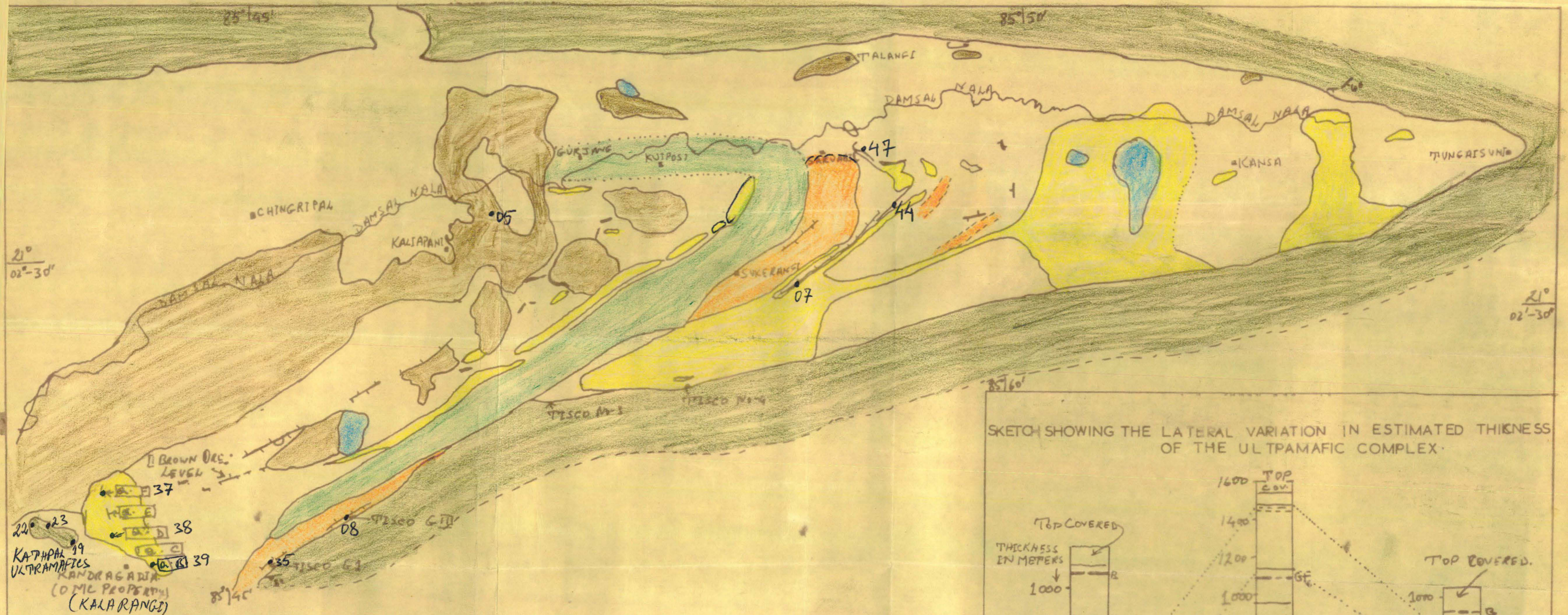
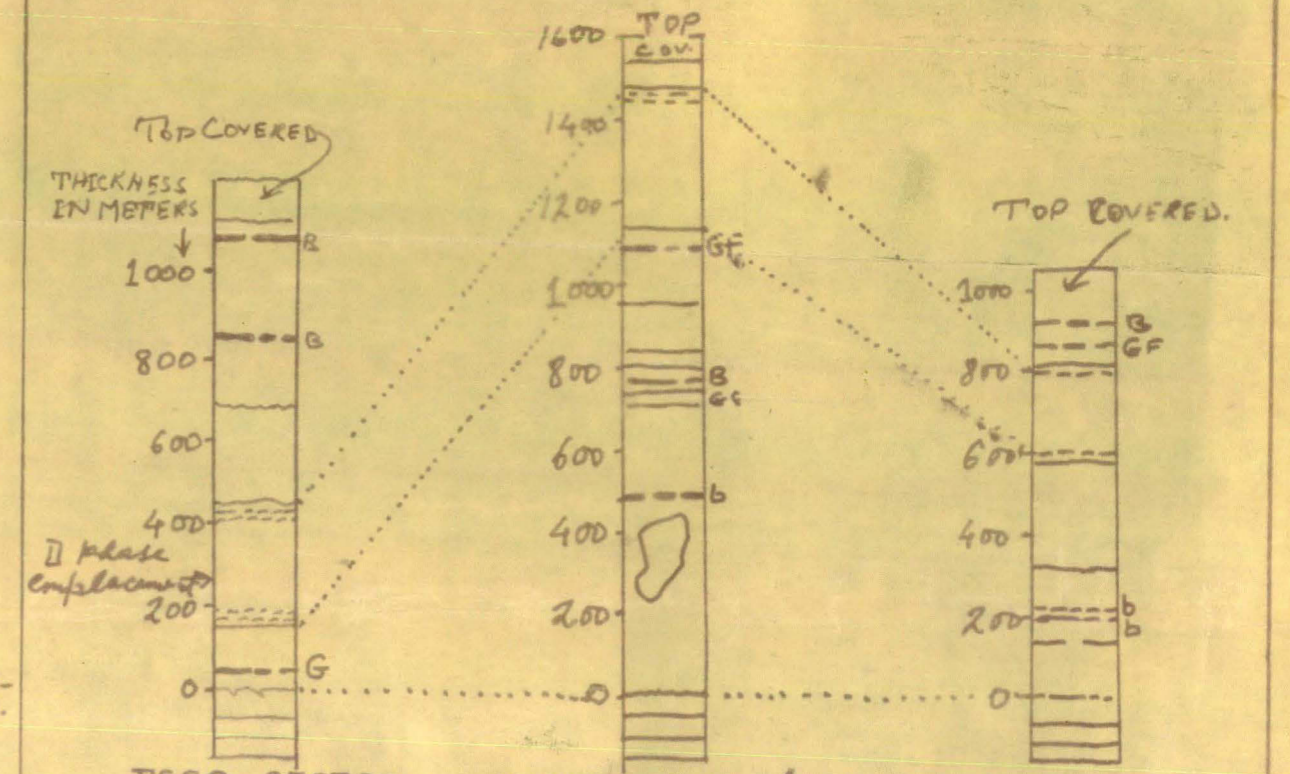


FIG.(3-1): GEOLOGICAL MAP OF THE SUKINDA ULTRAMAFIC-FIELD

- SOIL & ALLUVIUM MANTLE.
- LATERITE (Ct-BEARING).
- ORTHOPYROXENITE - MARGINALLY ALTERED.
- SILICIFIED ULTRAMAFICS.
- LIMONITISED ULTRAMAFICS.
- LOCALLY SILICIFIED SERP- ENTINITE/TALC SCHIST/ CHLORITE SCHIST.
- CHROMITITE.
- QUARTZITE.
- 60 STRIKE & DIPS OF FOLIATION.
- 60 STRIKE & DIPS OF LAYERINGS (S).

60 STRIKE & DIPS OF FOLIATION.
 CONTRAST CONTINUOUS APPROXIMATE, DOTTED WHERE CONCEALED.

SKETCH SHOWING THE LATERAL VARIATION IN ESTIMATED THICKNESS OF THE ULTRAMAFIC COMPLEX.



N.B. G- GREY MASSIVE CHROMITITE.
 B- CHROMITE-GOETHITE (AFTER SILICATES) ACCRETATE MAJOR-LAYERS.
 b- MINOR LAYER OF CHROMITE-GOETHITE.
 GF- GREY FRIABLE CHROMITITE.

The southern limb is exposed discontinuously and the hinge area is exposed by mining activities, but the northern limb is almost covered by hard pans of laterite and irregular spreads of conglomeratic wash. The Mahagiri and Daiteri hill ranges consisting of Cherty quartzite, surrounds the valley on its southern, northern and eastern parts. This quartzite was intruded by the chrome-rich ultramafic suite, near the northern base of the Mahagiri range at its western end. The chrome poor orthopyroxenite is free from any post-magmatic brecciation and silicification except that it has marginal alteration. Chatterjee and Banerjee (1964) have given the stratigraphic disposition of the various rock units of this area with the oldest rock at the bottom of the Column (Table 3-1).

Banerjee (1972) from his detailed studies of the area, has reported that the country rocks for the chromiferous ultramafites include contrasted types of metamorphic associations. North of the latitude $21^{\circ}00'$ the country rocks include green-schist facies quartzite and the ultramafites occur as concordant emplacements or as disjointed pendants, floating in biotite-granite. In contrast, south of latitude $20^{\circ}56'$, the ultramafites are distributed sporadically within a granulite facies assemblage and are very small in size. Banerjee has also reported that the granulite facies rocks immediately south of latitude $20^{\circ}56'$ mark the northern fringe of Mahanadi Valley Charnockite-Khondalite association in this area,

TABLE (3-1)




Alluvium and gravel ferruginous, Chromiferous & nickelferous laterite	
..... Unconformity	
Syn-and post orogenic	 Dolorite dykes and sills Granitic Complex
Early orogenic	 Chrome-poor pyroxenite and gabbros etc. <i>Chrome-</i> rich and hydrothermally altered ultramafites
Iron ore stage metasediments & metavolcanics	 Quartzites, banded hematite quartzite, epidiorite etc.

Table (3-1) - Stratigraphic succession of Sukinda Ultramafic Complex, after Chatterjee & Banerjee (1964).

and the green schist facies rocks north of latitude 21°00' are the southern out-post of the Iron-ore series of Bihar and Orissa. Thus, the ultramafic cluster of Sukinda Complex is located near the contact between two different stratigraphic-tectonic provinces (Banerjee, 1972). Mitra (1974) has observed that the quartzites at the northern foothills of Mahagiri are affected by shearings giving rise to cataclastic texture. The chromite grains were also deformed by the shearing movement and this caused cleavages in the chromite grains. These textural features appear to have been developed during the upward movement from depths where they crystallised (Mitra, 1974). Further, there is no evidence of contact metamorphism in the country rocks thereby suggesting that the intrusion was probably a "cold intrusion" in solid state.

Mineralogy of the ultramafic rocks and their hydrothermal derivatives:

The exposed rocks of ultramafic clan are divisible into two categories as follows:

First phase ultramafites: Petrographic studies have shown that chromite is the only primary mineral preserved in this suite (Banerjee, 1972). Different individual members of this rock suite are composed of an aggregate of hydrothermal minerals. Following are the rock types in this suite.

Serpentinite: This rock was found to occur sparsely in the lower and central portion of the area. It is a green, soft and fine grained rock with chrysotile, antigorite and montmorillonite as major minerals. Chromite is the predominant accessory ore mineral. Magnetite, haematite and goethite also are present as ill-defined grains or as dust like particles. *{ how ident. }*

Tremolite-schist: It is very rare and is found in small patches (three meters in length). It is a pale olive green, schistose rock with relict layering defined by chromite rich layer. The constituent minerals are tremolite, plagioclase, antigorite-lizardite, sphene and fine-grained, dispersely arranged chromite, in layers within the rock.

Talc-schist and serpentine-talc-schist: These are also rare rocks, pale apple green to milky white in colour. They are soft-schistose rock, composed of talc, antigorite and chromite minerals.

Chlorite-schist: These are very common, pale green to dark brownish green, schistose rock. They have minerals like clinochlore, penninite and chromite which occurs as accessory mineral having irregular outlines. Some goethite is also present.

In addition to the silicate assemblages, the major constituent rocks of first phase ultramafites are the limonitised and silicified rocks which are the end products of complete hydrothermal dissolution of the ultramafic silicates.

Second phase ultramafite-the orthopyroxenites: They are very well exposed as a tabular mass from near the TISCO Grade I quarry, north-eastwards upto Sukerangi village. They are very coarse grained, grey to pale green pyroxenite, the marginal facies of which is fine grained and better exposed along the southern flank. In thin section the pyroxenites seem to be made up of:

Enstatite - 95 to 98% of the total constituents.

Chromites - 2 to 4.7% of the total constituents.

These rocks are free from silicification and limotization unlike the first phase ultramafites.

Chromite deposits of Sukinda area: The bulk production, at present, comes from Saruabil Chromite Mines (SCM), Tata Iron & Steel Co. (TISCO) lease-holds and from Kalarangi-Kaliapani and Kathpal area of Orissa Mining Corporation (OMC). Banerjee (1972) has subdivided the chromite deposits of Sukinda into four kinds based on their geographical distribution.

(i) Kandragadia area (OMC lease-hold): This area lies to the west and south-west of TISCO lease-hold, covered superficially by hard lateritic soil. These are massive to friable chromite deposits exposed in six quarries of OMC, arranged more or less on the north-south trend. The ore bodies range in size from as small as a man's head to 100 x 5 to 7 meters (Banerjee, 1972).

(ii) Bhimatanagar area (TISCO lease-hold): The chromite deposits, in this area occur in three distinct sub-parallel stratigraphic levels. The ultramafic stratigraphy in this sector youngs northwards. The ore body in the lowest southernmost level, lying close to the ultramafic-quartzite contact, are known in this field as grey ore. They are in the form of lenses and discontinuous sheets of grey, hard, massive and medium grained chromite. The upper two ore bearing levels, exposed to its north, are known as the Brown ore bands. They are essentially brown to mauve, fairly soft and porous chromite-iron oxide aggregates, occurring as discontinuous sheets and lenses in sub-parallel levels. The overall trend of these ore bodies is N65°E, and dipping almost vertically.

(iii) Sukerangi-Saruabil-Kunardah area (Partly SCM and partly OMC lease-holds): The chromite deposits in this area are exposed in a number of levels, close to one another. The most prominent ore level is defined by the sickle shaped tabular grey and brown ore bodies. The northern arm of this sickle shaped ore level dips at 38° to 44° towards south, while the southern arm dips 70° to 83° towards north-west, giving rise to a synformal structure. Much of this ore level is composed of coarse, friable grey chromites.

(iv) The Gurjang-Kuiposi area (OMC lease-hold): Here the chromite deposits are lenticular bodies, hidden beneath a mantle of laterite and soil. The ore is brown coloured, soft and porous. The lenticular chromite ore bodies have an overall east-west trend with a dip of about 40° towards south.

Based on the modes of occurrence, Banerjee (1972) has classified the Sukinda chromite ores as follows:

1. Massive ore: They are almost pure chromite ore, without any primary or hydrothermal silicates in their matrix. The aggregate is hard and lumpy.
2. Friable ore: They are also monominerallic chromite bodies, without any interstitial gangue mineral. They crumble to a fine granular mass when pressed between fingers even with a mild pressure.
3. Banded ore: They are rare ore types, showing alternate bands of chromite-rich and silicate rich layers.
4. Spotted ore: The silicate minerals in these ores occur as oval or rounded spots within the chromite. Locally, the friable ore bodies are also spotted in nature.

The two types of chromite deposits namely the grey ore and brown ore, show conspicuous differences, in mineralogy, hardness and mode of occurrence as shown in Table (3-2) after Mitra (1974).

TABLE (3-2)

Properties	Brown ore zone	Grey ore zone
Colour	Brown	Steel grey
Physical constitution	Soft and friable	Hard and compact
Crystallinity	Coarse crystalline (Maximum size 4 mm)	Fine to medium
Common associates and matrix minerals	Chlorite (Kammererite), quartz, uvarovite, hydro-uvarovite (and never with any primary mineral or serpentine and rarely with talc)	Serpentine, talc rarely with olivine and/or enstatite and rarely with chlorite or anthophyllite
Host environment	High alumina rocks (Shale, chlorite-schist etc.)	High magnesia rocks (Serpentine, talc-schist etc.)
Proximity to mafic and marginal intrusives	Far	Nearer
Euhedralism	>50%	<50%
Specific gravity	3.4 - 4.5	4.5 - 5.1
Chemical composition of the chromite separates:		
Constituents:		
SiO ₂ %	0.57 - 1.14	0.08 - 0.5
Cr ₂ O ₃ %	57.34 - 62.74	54.73 - 59.74
Al ₂ O ₃ %	11.09 - 13.03	12.61 - 14.95
MgO %	11.97 - 14.3	11.38 - 15.47
FeO %	12.51 - 15.59	12.20 - 15.95
CaO %	0.01 - 0.03	0.02 - 0.12
TiO ₂ %	0.19 - 0.33	0.02 - 1.30
Zoning	Cr & Fe increase and fall in Mg, Al in contact with Kammererite	Increase in Fe only in contact with serpentine
Cell-size	Mean Value 8.23 Å	Mean Value 8.30 Å
Reflectance	Mean Value 13.694	Mean Value 13.198

Table (3-2) - Comparison of characters of chromites from two ore zone, after Mitra (1974).

Mineralogy of chromite ore and the associate gangue minerals

The chromite is the only primary mineral and all the gangue minerals are products of hydrothermal alteration. The grey and brown ore have contrasting association of gangue minerals.

Grey Ore: ~~This~~ ore has the following mineralogy:

1. Chromite: They are steel grey to black in colour. The grains have well developed octahedral and dodecahedral faces even in the friable ore bodies. In polished sections the ore is made up of idiomorphic to hypidiomorphic, greyish brown chromite, extensively cut by fracture surfaces.
2. Uvarovite: Bright green, fine grained minerals, occupying the non-penetrative surfaces within the grey ore bodies. Under microscope they occur as an aggregate without any developed crystal faces. They are associated with only massive grey ore and are absent both in the friable and the brown ores.
3. Chromium chlorite: This mineral is lavender coloured, flaky, fine to coarse grained. It is colourless in thin section. They occur as fracture fillings in the chromitite seams, of both massive and friable ores. According to Banerjee (1972), the Cr_2O_3 content of a purified chromium chlorite is about 1.82%.

4. Magnetite & Haematite: In polished sections, micro-veins of magnetite and haematite, varying in thickness from hair-thin flake to irregular pools traverse the chromite crystals, along the fracture surfaces, in both massive and friable ores. Magnetite being greyish brown in reflected light, are isotropic, embays into chromite and is devoid of any crystal faces. Haematite is more abundant than magnetite and appears bright white in reflected light.

5. Silica: The chromite ore bodies are frequently traversed by veinlets of opaline to crystalline and vuggy quartz. Locally, they engulf triangular to polygonal fragments of chromite. In some of the joint infillings within the massive ore bodies, a central core of vuggy quartz is lined on either sides by films of uvarovite and chromium chlorite. This suggests silicification post-dated all other gangue minerals.

Brown ore: The brown ore bodies are composed of the following minerals:

1. Chromite: They have the same optical properties as the grey chromite ore. They have more than two sets of fracture planes. Crystals are hypidiomorphic to xenomorphic with feebly to strongly resorbed margins, at places assuming cuneiform outlines.
2. Haematite: They are in form of veinlets, and appear bright white and anisotropic under reflected light. They are intimately

associated with goethite and they are dominant in the lower brown ore levels.

3. Goethite: They are anisotropic under reflected light and they occur as veinlets and pools of variable dimensions, they embody both chromite and haematite, sometimes they show colloform banding.

4. Kaolinite: This is soft, white and earthy in hand specimens. They are in form of veinlets across chromite-iron oxide aggregate or as mottled mauve-and-white goethite-kaolinite aggregate, veining the brown ore bodies.

5. Opaline and crystalline silica: This is common as thin ribs and anastomosing network, cutting across all other minerals.

Chemistry of chromite ores from Sukinda:

Sukinda ultramafic complex, being the largest chromiferous field in India, and on account of wide diversity in their mineralogical, structural and petrographic characters, this area has been studied in detail by many workers earlier, including Banerjee (1961-72), Mitra (1958-76), Chakraborty & Baidya (1978). These studies help us in terms of understanding the nature of parental magma and the physico-chemical conditions prevailed during its crystallisation. The above two factors are particularly useful to decipher the origin of the chromite deposits. Some of the

published chemical analysis are included in Tables (3-3 to 3-10) for convenience, and the present discussion (Chapter 5) has been based on all these published data.

According to Mitra (1976) the cumulus chromites are often subjected to chemical readjustment along the grain boundary due to changes in the chemistry of the magma and interstitial liquid during the process of crystallisation and segregation of the ore minerals. Generally it is reflected by the overgrowths of iron-rich members of chromite-magnetite-haematite-limonite series. Further he suggests that wider variability and distinctly different phases, than the normal crystallisation phases, are possible because of hydrothermal metasomatism and weathering of the chromite. Banerjee (1972) based on his analytical data, has pointed out certain important features for the Sukinda Chromites which are as follows:

The $\text{Fe}_2\text{O}_3:\text{FeO}$ ratio, which is an indicator of partial pressure of oxygen in the magma, during the course of crystallisation was varying vertically and horizontally, indicating that there was high oxygen fugacity at the earliest stages of crystallisation, when the lowest grey massive ore was crystallising and the oxygen fugacity was decreasing with the progressive crystallisation, as shown in Table (3-8).

TABLE (3-3)

Constituents	1	2	3	4	5	6	7	8
Cr ₂ O ₃	55.54	55.24	54.77	59.54	61.10	60.60	61.02	62.61
Al ₂ O ₃	5.72	10.55	8.82	12.43	11.56	6.81	12.25	9.72
FeO	7.07	10.88	11.48	12.70	13.05	13.68	13.45	13.24
Fe ₂ O ₃	14.17	3.16	7.96	1.47	0.60	5.15	Nil	1.10
MgO	16.71	16.10	14.76	13.96	13.66	12.38	33.28	13.31
SiO ₂	0.72	3.84	1.74	0.25	0.10	Tr.	Tr.	0.11
CaO	n.d.	Tr.	Tr.	-	n.d.	n.d.	n.d.	n.d.

- No. 1: TISCO Grade I. Chromite ore body \downarrow Grey and massive ores.
 No. 2: TISCO Grade III. Chromite ore body \downarrow
 No. 3: SCM Quarry No. 5b
 No. 4: SCM Quarry No. 4
 No. 5: Lower brown ore, SCM Quarry No. 6.
 No. 6: Grey and Friable ore, Kuiposi ore body OMC.
 No. 7: Middle brown ore, TISCO area.
 No. 8: Upper brown ore TISCO area.

Table (3-3) - Chemical analysis of chromite separates from different areas, after Banerjee (1972).

TABLE (3-4)

Constituents	TISCO Grade I		SCM Quarry No. 4		Kuiposi Ore	
	Lower	Upper	Lower	Upper	Lower	Upper
Cr_2O_3	55.54	59.11	56.20	53.82	60.60	61.49
Al_2O_3	5.72	8.98	11.11	11.83	6.31	8.72
Fe_2O_3 as total Fe	22.03	16.26	14.40	16.57	20.36	17.41
MgO	16.71	15.61	12.45	12.09	12.23	12.38
SiO_2	0.45	0.89	3.21	3.00	0.13	Tr.

Table (3-4) - Partial chemical analysis data showing vertical variation in chromite chemistry, after Banerjee (1972).

TABLE (3-5)

Elements	1	2	3	4	5	6
Cr	38.22	36.40	12 - 34	31 - 38	7 - 29	42 - 44.29
Fe	11.02	9.31	11 - 18	13 - 21	14 - 24	20.61 - 24.99
Cr:Fe	3.4	3.8	1 - 2	1.4 - 3	0.3 - 1.2	1.8 - 2.1

No. 1: TISCO Grade I Quarry, grey massive ore.

No. 2: TISCO Grade III Quarry, grey massive ore.

No. 3: SCM Quarry 6, lower brown ore.

No. 4: TISCO area, middle brown ore bodies (with TISCO borehole pillars 8F, 39F & 47F).

No. 5: TISCO area upper brown ore bodies (TISCO borehole pillars 31F, 2F, 4F).

No. 6: OMC area, Kuiposi friable ore (borehole sample).

Table (3-5) - Partial analysis of grab samples of ores from different levels, after Banerjee (1972).

TABLE (3-6)

Oxides	1	2	3	4	5	6	7	8
SiO ₂	0.57	1.21	0.27	0.86	0.53	1.14	0.08	0.25
Cr ₂ O ₃	62.74	58.86	58.45	62.13	57.34	59.94	59.74	54.89
Al ₂ O ₃	11.72	12.16	15.63	11.09	13.03	12.58	12.61	14.95
MgO	12.04	11.97	11.43	13.10	14.33	12.60	11.38	15.47
FeO as total Fe	12.54	15.59	13.87	12.57	14.73	13.50	15.95	12.20
CaO	0.01	0.02	0.01	0.02	0.03	0.03	0.02	0.12
TiO ₂	0.21	0.19	0.33	0.23	0.02	0.21	0.22	1.30
Total	99.80	100.00	99.99	100.00	100.01	100.00	100.00	99.88

No. 1: Brown ore from Quarry No. 4 of SCM. Coarse euhedral chromite with lattice matrix chlorite, limonite & goethite.

No. 2: Brown ore from Quarry No. 5 of SCM-coarse euhedral chromite with lattice matrix chlorite, limonite & goethite.

No. 3: Coarsest grain of chromite (1 cm. across) in the brown ore zone near Sukerangi village, matrix composed of limonite & goethite with chlorite.

No. 4: Contains highly decomposed and limonitised ore with isolated small rounded grains of chromite, from SCM Quarry No. 3B.

No. 5: Brown ore collected from a matrix of talc & silica.

No. 6: Brown ore collected from Quarry No. 6 of SCM.

No. 7: Grey ore, collected from near Bhimtanagar village, associated with serpentine.

No. 8: Grey ore collected from foothills of the Mahagiri in the south of Marmabil, associated with spots of spherulitic autophyllite.

Table (3-6) - Geochemical analysis of Sukinda chromites,
after Mitra (1976).

TABLE (3-7)

Oxides	Sample No. Q. 1	Sample No. Q. 2	Sample No. FA-Q. 4
SiO ₂	0.52	0.52	0.90
Al ₂ O ₃	10.88	12.59	11.23
Cr ₂ O ₃	58.95	57.00	56.86
Fe ₂ O ₃	0.05	0.08	0.07
TiO ₂	0.28	0.24	0.28
FeO	12.35	12.88	11.82
MgO	14.50	13.76	14.48
MnO	0.17	0.17	0.16
NiO	0.11	0.13	0.09
CaO	0.67	0.23	0.88
(Na ₂ O + K ₂ O)	0.23	0.27	0.19
H ₂ O (free & combined)	0.96	1.04	3.30
Total	99.67	99.91	100.26

Table (3-7) - Chemical composition of Kathpal chromites of the Sukinda chromites belt, after Chakraborty & Baidya (1978).

TABLE (3-8)

Ore levels	Fe_2O_3 %	$\text{Fe}_2\text{O}_3:\text{FeO}$
Upper brown ore	1.10	0.083
Upper friable ore (Kuiposi)	5.15	0.379
Lower brown ore	0.60	0.043
Lower friable ore (SCM)	1.47 - 7.96	0.115 - 0.693
Grey massive ore	3.16 - 14.17	0.290 - 2.00

Table (3-8) - Variation of Fe_2O_3 % and $\text{Fe}_2\text{O}_3:\text{FeO}$ ratio in the Sukinda chromites, after Banerjee (1972).

TABLE (3-9)

Ore levels	MgO/FeO
Upper brown ore	1
Middle brown ore	1
Upper friable ore	0.905
Lower brown ore	1.04
Lower friable ore	1.10 - 1.26
Lowest grey & massive ore	1.48 - 2.36

Table (3-9) - Variation of MgO/FeO for
different ore levels in Sukinda,
after Banerjee (1972).

TABLE (3-10)

Ore levels	$\text{Cr}_2\text{O}_3 : \text{Al}_2\text{O}_3$	$(\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3)\%$
Upper brown ore	6.4	72.53
Middle brown ore	4.9	73.27
Upper friable ore	8.9	67.41
Lower brown ore	5.3	72.66
Lower friable ore	4.8 - 6.2	63.59 - 71.91
Grey massive ore	5.2 - 9.7	61.26 - 65.79

Table (3-10) - Table showing increase in $(\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3)$ of the total R_2O_3 for different ore levels, after Banerjee (1972).

The MgO/FeO ratio, which could be considered as an index of progressive crystallisation, show a fairly steady trend of variation from the lowest to the highest ore levels as shown in Table (3-9). This variation is in accordance with the theoretical expectations of early chromite being richer in MgO than the fractions crystallising later from the same melt. The Al_2O_3 : MgO ratio, was found to show no systematic variation. The Cr_2O_3 and Al_2O_3 content of gangue-free chromite do not show any apparent relationship, as reported elsewhere (Thayer, 1964). But in Sukinda the $(Cr_2O_3 + Al_2O_3)$ in chromites increases towards stratigraphically higher levels, as shown in Table (3-10). The erraticity in Cr_2O_3 : Al_2O_3 values, according to Banerjee (1972) is reflection of varying Fe-oxidation conditions during the crystallisation of chromite, a reciprocal relation between Cr_2O_3 and Al_2O_3 is marked by accommodation of varying quantity of Fe_2O_3 in the total R_2O_3 group.

To sum up, the chemical characteristics of the chromite ore bodies, except for decreasing MgO:FeO ratio towards upper stratigraphic ore levels, (do not show either any uniformity or any *As expected* progressive lateral or vertical variation which are characteristics of stratiform complex. Mitra (1973) based on his studies on the olivine separates, suggested alpine peridotite source, as no

fayalite-rich (Fe rich olivine) fractionates are present in this area and the high forsterite content in early settled olivines indicates an alpine peridotite source. Also Banerjee (1972) from his detailed studies suggested alpine type orogeny for the origin of Sukinda ultramafic complex.

CHAPTER 4

The field work for the present study was carried out in July 1978 when ore samples were collected from working pits and other exposed chromite bands. The sample locations are shown in the map (Fig. 3-1). Care was taken in selecting the samples so that they represent the entire chromite field of Sukinda. The localities from where the samples were taken are given in Table (4-1).

The samples were first prepared for the chemical analysis. As we were interested in getting pure chromite grains for the chemical analysis, mineral separation was carried out by eliminating other minerals associated with the chromite ore. The separation was a very rigorous and time consuming task. It was done as follows by different methods, at different stages, to get the purity of the ore to the extent of $>95\%$, as indicated by the x-ray diffractogram.

Comminution or size reduction: The first step taken was comminution. About 100 gms of representative samples were taken and were crushed. They were sieved into four different sizes:

- i) -60 + 72 mesh
- ii) -72 + 86 mesh
- iii) -86 + 100 mesh
- iv) -100 + 200 mesh.

The comminution was done to separate the interlocking minerals associated with chromite crystals.

TABLE (4-1)

Serial No.	Sample No.	Localities
01	05	Kalipani, Quarry No. 1
02	07	Sukerangi Chromite Mine, Quarry No. 1
03	08	TISCO Grade 3 Quarry
04	19	Kathpal, Quarry No. A
05	22	Kathpal, Quarry No. G
06	23	Kathpal, Quarry No. E
07	35	TISCO, Grade 1 Quarry
08	37	Kalarangi, Quarry No. F
09	38	Kalarangi, Quarry No. D
10	39	Kalarangi, Quarry No. B
11	44	Saruabil Chromite Mines, Quarry No. 4
12	47	Saruabil Chromite Mines, Quarry No. 1

Table (4-1) - Sample locations for the present study
on Sukinda chromite belt.

Heavy liquids separation: It was based on the density differences, in it the density of the used liquid is such that the wanted minerals either sink or float in the liquid while the unwanted minerals behave in the reverse manner. The possible associated minerals with the chromite ore are given in Table (4-2).

Taking into consideration, the specific gravity of the chromite ore and the possible associated minerals, three heavy liquids were used (Table 4-3), one after the other with increasing densities.

After treating with the Clerici's solution the separated ore was washed with hot water and acetone and was dried under infra-red lamps.

Magnetic separation: The dried samples were further purified by magnetic separation. For this, a hand magnet was used to get rid of any magnetite associated with the ore samples.

Microscopic separation: The final purification of the ore samples was done by hand picking under a binocular microscope so that the fraction obtained was almost pure chromite. The confirmation of the purity, of the ore samples, was done by taking an x-ray diffractogram. Only chromite peaks were present in the diffractogram (Table 4-4). This confirmed the purity of the separated ore to be $> 95\%$.

TABLE (4-2)

Minerals	Specific gravity
Serpentine	2.6
Olivine (Forsteritic)	3.2
Sphene	3.54
Uvarovite	3.43
Chlorite	2.65 - 2.94
Magnetite-Haematite	5.18
Chromite	4.5 - 4.8

Table (4-2) - Possible minerals associated with the chromite samples of Sukinda chromite belt.

TABLE (4-3)

Heavy liquids	Densities (in gm/ml at 20°C)
Bromoform	2.89
Methylene iodide (di -iodomethene)	3.325
Clerici's solution	4.28

Table (4-3) - The three heavy liquids used to separate the pure chromite.

TABLE (4-4)

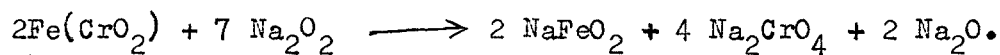
Sample 44/ -72 d values	Sample 44/ -86 d values	d values for chromites from ASTM cards nos:	
		4-0759	3-0873
4.7663	4.8176	4.83	4.82
3.0153	2.9284	2.95	2.95
2.4926	2.5060	2.51	2.52
2.3800	2.3779	2.08	2.40
2.0741	2.0696	1.91	2.07
1.6879	1.8954	1.71	1.69
1.5963	1.6924	1.61	1.60
1.4576	1.5963	1.49	1.46
1.4000	1.4596	1.33	1.40
1.2624	1.3992	1.28	1.3
1.1946	1.2653	1.21	1.26
1.1575	1.2483	1.17	1.20
1.1060	1.1946	1.12	1.16
1.0771	1.120	1.08	1.11
0.95634	1.0771	1.05	1.10
0.92529	1.0347	0.965	1.04
	0.9555	0.933	0.979
	0.94908	0.873	0.960
	0.9255	0.854	0.931
	0.9085		0.873
	0.9060		0.850
	0.8780		0.815
	0.86758		0.805

Table (4-4) - d Values for the chromite peaks in sample 44 (originally ground to -72 and -86 mesh) as shown by the x-ray diffractogram, and d values for chromites from ASTM card numbers 4-0759 and 3-0873.

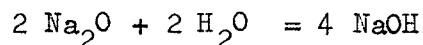
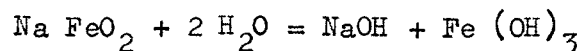
Chemical analysis: The chromite samples were analysed chemically as follows:

Determination of chromium in the chromite ore samples:

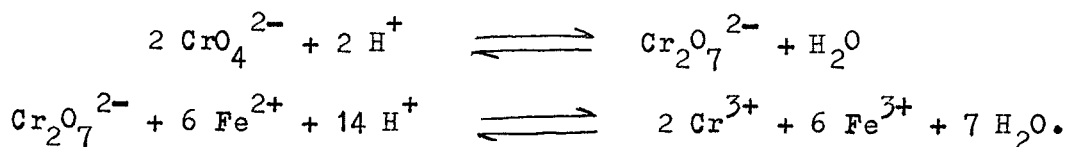
The powdered chromite ore (-100 mesh) which is highly refractory was taken in a nickel crucible and was brought into solution by fusion with excess of sodium peroxide with the following reaction:



Then upon leaching the melt with water, the sodium chromate got dissolved and the iron was precipitated as ferric hydroxide.

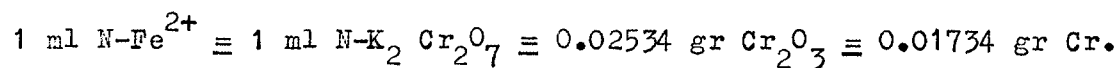


The excess of peroxide was decomposed by boiling the alkaline solution. The precipitate was filtered off after diluting the solution and the filtrate was acidified with HCl. A known volume of excess ferrous ammonium sulphate solution (50 ml of 0.1 N-ferrous ammonium sulphate) was added, and the excess of ferrous salt was titrated with standard dichromate solution:



Procedure: 0.5 gm of sample powder was taken in a nickel crucible, 4 gm of sodium peroxide was added to it and was mixed thoroughly by means of a thin glass rod. This thin glass rod was later stirred in 1 gm sodium peroxide, to remove any ore powder adhering to the rod. This was also transferred to the crucible. The crucible was covered by the nickel lid and was heated over a small flame, for ten minutes to get the mass quite liquid, it was heated for another ten minutes at a dull red heat. It was kept for cooling and a solid crust was formed. 4 gms of sodium peroxide was again added and the mixture was fused at cherry-red heat for ten minutes. The crucible was kept for cooling and then was placed in a 1000 ml beaker containing a little distilled water. The beaker was covered by a glass cover and a little warm water was added to the crucible and a violent action in the crucible was observed. The set up was left overnight for complete dissolution of the fused mass. The crucible was removed after washing it thoroughly, collecting the washing in the same beaker. The liquid was boiled for 30 minutes, keeping the beaker covered, to decompose the excess sodium peroxide. 250 ml of boiling water was added to the boiling solution, and the precipitate was allowed to settle. This was filtered through millipore filter paper and the residue was washed thoroughly with boiling water, until it was free from chromate (indicated by colourless distilled water passing through the filter paper). The residue was checked for

complete solubility in concentrated HCl and no black gritty particles remained, indicating complete decomposition. The filtrate was evaporated to about 200 ml, then was cooled and 9 N-sulphuric acid was added to make it acidic. It was cooled and transferred to a 250 ml measuring flask, and made up to the mark with distilled water. It was shaken very well and 50 ml of this solution was removed with a pipette to a 250 ml beaker. 50 ml of 0.1 N-ferrous ammonium sulphate solution, 5 ml of syrup phosphoric acid and 0.4 ml of sodium diphenylamine sulphonate indicator were added and was diluted to 200 ml. This solution was titrated with standard 0.1 N-potassium dichromate until the green colour changed to violet-blue. Three titrations were done for each sample, and the mean value was taken. The ferrous ammonium sulphate solution was standardised by titration with the 0.1 N-potassium dichromate and sodium diphenylamine sulphonate was used as indicator. The volume of the ferrous solution was calculated, which was oxidised by the dichromate originating from the chromite and from this the percentage of chromium in the original ore was calculated.



From this chromium value of Cr_2O_3 percentage was calculated for each sample (Table 4-5).

Determination of MgO, FeO & Al₂O₃ in chromite ore samples:

The chromite ore was made into solution by H₂SO₄ and HClO₄ and chromium was removed by volatilization of CrO₂Cl₂. The SiO₂ was separated and all insoluble oxides were recovered from it. After a double R₂O₃ separation, iron was separated with sodium hydroxide and aluminium with 5% oxine solution and 40% ammonium acetate solution to get Al (C₉H₆ON)₃, from this Al₂O₃ in the samples were calculated.

Procedure: 1 gm of sample powder was taken into a 250 ml beaker and 50 ml of H₂SO₄ (1:4), 5 gm of (NH₄)₂SO₄ and 20 ml of HClO₄ were added to it. The beaker was covered by a watch glass and was heated gently till fumes of HClO₄ started evolving freely and the chromium was oxidized to chromic acid. The watch-glass was removed. With continuous heating, chromium was volatilized as CrO₂Cl₂ by adding small portion of NaCl. The CrO₂Cl₂ gave dense brownish very pungent fumes and it continued till all the chromium was volatilized. It was cooled to some extent and 75 ml of water was added and the solution was boiled for 10 minutes. It was filtered on 11 cm filter paper containing a little paper pulp and the filtrate was caught in a 500 ml beaker. This was washed thoroughly with hot water. The paper was ignited in a platinum crucible at a dull red heat till the carbon had burnt off completely. It was cooled and 5 ml of HF, 2 ml of HNO₃ and 0.5 ml of H₂SO₄ (1:1)

was added. The solution was evaporated to dryness to volatilize the silica and other insoluble oxides. The residue was fused with 1.5 gm of $\text{Na}_2\text{S}_2\text{O}_7$ and after cooling, it was dissolved in 25 ml of hot HCl (1:9) and was added to the filtrate by washing the platinum crucible, after filtering it.

F_2O_3 separation: 5 gm of NH_4Cl was added and the solution was heated just to boiling. A very faint excess of diluted NH_4OH (1:2) was added and it was heated again to boiling for 1 minute and 30 seconds. The precipitate was allowed to settle, it was filtered on 11 cm paper containing a little paper pulp, and was washed 10 times with hot NH_4Cl solution (20 gm/liter neutralized with NH_4OH). The paper and precipitate was returned to the original beaker and was treated with 50 ml of HCl (1:4). It was heated to boiling and was then diluted to 100 ml with hot water, and it was precipitated again with NH_4OH , again filtered it and washed thoroughly with NH_4Cl solution. The two filtrates were combined for the determination of magnesium oxide.

MgO determination: The filtrate was acidified with HCl and then was evaporated to a volume approximately 250 ml, it was cooled to 15°C . 50 ml of diammonium phosphate solution (100 gm/liter) was added to it and NH_4OH was added slowly with vigorous stirring till the solution was ammonical and a crystalline precipitate appeared. An excess of 25 ml of NH_4OH was added and the liquid was stirred

thoroughly and finally was cooled to room temperature. It was allowed to stand overnight. It was filtered on an 11 cm filter paper containing a little paper pulp and was washed thoroughly by decantation with cold NH_4OH (2:98). 25 ml of HCl (1:1) was poured through the filter, and was collected in the original beaker containing the bulk of precipitate. The filter paper was washed thoroughly with hot HCl (5:9). It was diluted to a volume of 150 ml with cold water and was cooled to room temperature. 3 ml of diammonium phosphate solution was added and at room temperature, NH_4OH was added slowly and crystalline precipitate appeared again. It was filtered and then was washed thoroughly with cold NH_4OH (2:98) and then twice with a cold NH_4NO_3 solution (50 gm/liter). The precipitate and filter paper was ignited in a weighed platinum crucible at a dull red heat till the carbon had burnt and finally to constant weight (approx. 30 minutes), then was kept in the desiccator for 30 minutes and was then weighed as $\text{Mg}_2\text{P}_2\text{O}_7 + \text{Ca}_3(\text{PO}_4)_2 + \text{MnP}_2\text{O}_7$. The $\text{MgO}\%$ (Table 4-5) was calculated as follows:

$$\text{MgO}\% = \frac{\text{A} \times 0.3622}{\text{B}}$$

where $\text{A} = \text{Weight of } \text{Mg}_2\text{P}_2\text{O}_7^*$

$\text{B} = \text{Weight of ore samples.}$

*Assuming the amount of $\text{Ca}(\text{PO}_4)_2 + \text{MnP}_2\text{O}_7$ was negligible.

Determination of total Iron in the form of FeO:

The NH_4OH precipitate in the filter paper was returned to the original beaker by dissolving the precipitate with HCl and was thoroughly washed by HCl (1:2). Iron was precipitated by NaOH saturated solution and the precipitate was allowed to settle down. It was filtered and washed thoroughly, the filtrate being reserved for Al_2O_3 determination. The precipitate was again dissolved by HCl and was washed thoroughly catching the solution into a 500 ml beaker. It was heated to boiling and then iron was reduced with SnCl_2 solution (50 gm/liter of HCl). 2 drops in excess was added. It was cooled to $< 20^\circ\text{C}$, 10 ml of saturated HgCl_2 solution was added and was stirred well. It was then allowed to stand for 2 minutes, then diluted to 200 ml with cold water, 5 ml of H_3PO_4 , and 10 ml of H_2SO_4 (1:1). A few drops of sodium diphenylamine sulphonate indicator was added and was titrated with 0.1-N $\text{K}_2\text{Cr}_2\text{O}_7$ to a purple end point. FeO percentages (Total Iron) for each samples were calculated as:

$$\text{FeO}\% = \frac{A \times 0.007185}{B} \times 100$$

where A = ml of 0.1-N $\text{K}_2\text{Cr}_2\text{O}_7$

B = Weight of samples in gms.

Separate FeO and Fe_2O_3 concentrations in the ore samples were recalculated from the total iron (as FeO calculated earlier), on the basis of spinel stoichiometry, i.e., on the basis of 32 oxygen in the structure. The FeO and Fe_2O_3 percentages for the samples are given in Table (4-5).

Al₂O₃ determination: Few drops of methyl red indicator was added to the filtrate from NaOH and this was neutralized with HCl (1:1) to the colour change of methyl red indicator and then 4 ml excess of HCl (1:1) was added. The volume was brought to about 200 ml, 5 ml of 50% hydroxyl ammonium chloride solution and 3 ml of 1% O-phenanthroline solution in 1:1 acetic acid was added, to make complex of any residual iron. 20 ml of 5% oxine solution in dilute acetic acid (1:8) followed by 40 ml of 40% ammonium acetate solution was added slowly with stirring. It was heated to 70°C for 10 minutes and then cooled for 30 minutes, the precipitate was collected on a weighed sintered with water. It was dried at 135°C to complete dryness, then was kept in a desicator for 30 minutes and weighed as Al(C₉H₆ON)₃. The Al₂O₃% (Table 4-5) was calculated from it as follows:

$$\text{Al}(\text{C}_9\text{H}_6\text{ON})_3 = a \text{ gms}$$

$$\text{or } 27(108 + 6 + 16 + 14)_3 = a \text{ gm or } 459 = a \text{ gms}$$

$$\text{and } \frac{102}{459} = .222 / \therefore \text{Al}_2\text{O}_3 = 54 + 48 = 102$$

- 1 gm samples contain a gm Al(C₉H₆ON)₃
- a gm Al(C₉H₆ON)₃ has a x .222 gm Al₂O₃,
- Al₂O₃% = a x .222 x 100.

Different elements concentrations (Table 4-6) in the chromite ore samples were calculated from the values of different oxides (Table 4-5), on the basis of spinel stoichiometry.

TABLE (4-5)

Sample No.	MgO%	FeO%	Cr ₂ O ₃ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	Total
05	14.34	9.91	63.09	11.76	-	99.12
07	16.75	8.34	59.03	14.02	1.14	99.28
08	20.25	2.30	52.62	15.16	8.47	98.80
19	17.93	5.65	56.92	12.05	6.56	99.11
22	14.48	11.76	62.50	11.31	0.16	100.21
23	16.52	7.39	57.09	9.99	8.41	99.40
35	17.13	7.57	62.07	10.71	3.63	101.11
37	17.15	7.87	63.85	10.46	2.61	101.74
38	15.71	7.83	62.33	11.37	1.58	98.82
39	17.97	5.48	61.32	10.61	3.14	98.52
44	16.31	8.54	64.61	8.91	2.38	100.75
47	17.03	7.32	62.08	9.45	4.96	100.84

Table (4-5) - Chemical analyses results for the present study on Sukinda Chromite ore samples.

TABLE (4-6)

Sample No.	Mg ²⁺	Fe ²⁺	Total of Bivalent ions	Cr ³⁺	Al ³⁺	Fe ³⁺	Total of Trivalent ions
07	6.2536	1.7464	8.0000	11.5752	4.0984	0.2392	15.9128
08	7.5216	0.4784	8.0000	10.2632	4.4096	1.7664	16.4392
19	6.8000	1.2000	8.0000	11.3376	3.5748	1.3976	16.3136
22	5.4952	2.5048	8.0000	12.4568	3.3608	0.0336	15.8512
23	6.3952	1.6048	8.0000	11.6016	3.0624	1.8280	16.4920
35	6.4096	1.5904	8.0000	12.1976	3.1376	0.7616	16.0968
37	6.3629	1.6376	8.0000	12.4400	3.0384	0.5448	16.0232
38	5.9528	2.0472	8.0000	12.4048	3.3728	0.0920	15.8696
39	6.8304	1.1696	8.0000	12.2384	3.1592	0.6696	16.0672
44	6.1824	1.8176	8.0000	12.8608	2.6448	0.5056	16.0112
47	6.4464	1.5536	8.0000	12.3416	2.8008	1.0544	16.1968

Table (4-6) - Concentration of different elements in the chromite ore samples from Sukinda.

Petrography of chromite samples

The polished section of ore samples were studied under reflected light to observe the texture of the ore so that chemistry of the ores can be discussed in terms of their textural features. Also the microscopic study was done very carefully to see whether any platinoid minerals or any other inclusion is present within chromite grains, as platinoid minerals generally occur as inclusion in chromite grains or between the grain boundaries of the chrome spinels (Crocket et. al., 1976). The description of different samples are as follows:

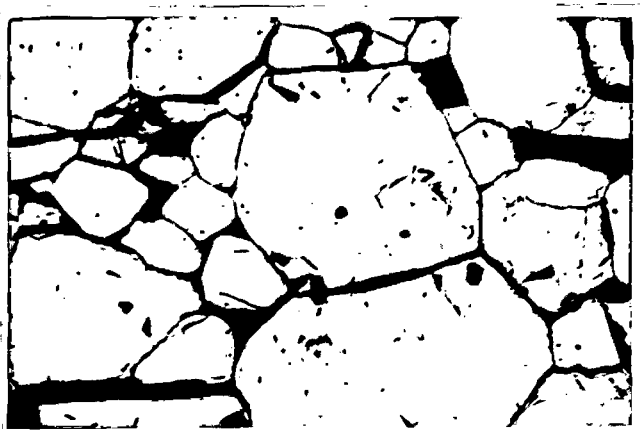
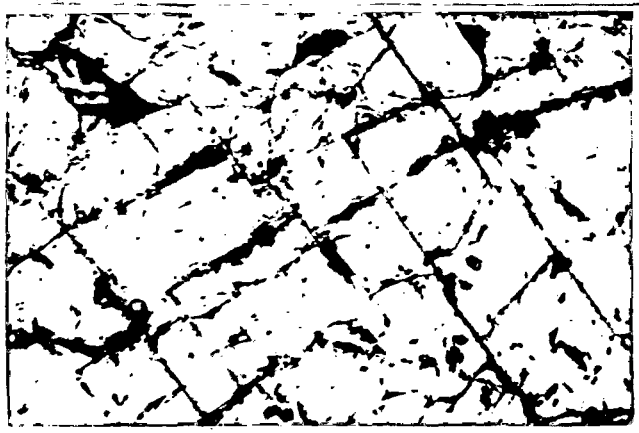
Sample 05:

Handspecimen: The ore is greyish-brown. It is coarse grained and some medium grained crystals are also associated with it. The admixture of coarse and medium grained chromites was observed in small handspecimen indicating uniform heterogeneity in grain size.

Polished section (Fig. 4-1): Coarse grained ore with well-developed cleavages or deformation planes. Very highly fractured. No inclusion was seen. It is a pure chromite ore. Crystal faces not very well developed or they are having corroded grain boundaries. The crystals are showing pull-apart texture, typically shown by podiform chromites because of tensional stress. Serpentine minerals are filling the irregularly developed fractures within chromite grains. The grain boundaries are touching each other with no or very little cementing materials.

Fig. (4-1): Chromite grain showing well developed cleavages. Serpentine (black coloured) filling up irregular fractures of pull-apart texture (Reflected light Mag. x 100).

Fig. (4-2): Chromite ore showing cumulus texture. The bigger grains have well developed faces and the smaller grains are rounded or corroded with very small amount of silicate matrix (Reflected light Mag. x 50).



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Sample 07:

Handspecimen: It is massive, very coarse grained hard ore, blackish to brown in colour.

Polished section (Fig. 4-2): The ore is crystalline. The polished section shows typical cumulus texture with medium to coarse grained chromite crystals settled in a matrix of silicate minerals. The coarse grained chromite crystals have well developed faces, but the edges for both the coarse and medium grained crystals are rounded or corroded. The crystal boundaries are separated by small amount of matrix material.

Sample 08:

Handspecimen: This is hard, lumpy ore. Grey in colour. It has bands of green coloured minerals, probably serpentine.

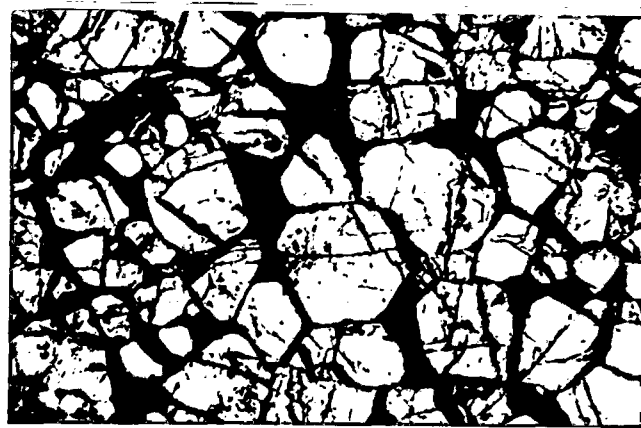
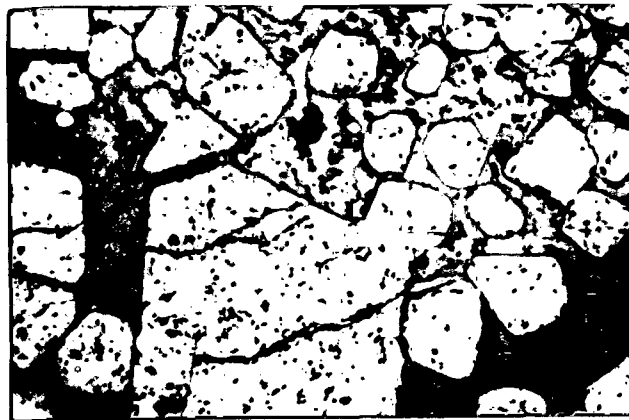
Polished section (Fig. 4-3): Coarse grained ore with typical cumulus texture consisting of euhedral chromite crystals with good amount of silicate matrix. Some of the chromite grains are very coarse grained while most of them are medium to fine grained, with less developed faces and more corroded edges, as compared to the coarse grained chromite crystals. The chromite is showing bright fringing zones or solutions, probably developed due to differentiation during the crystallisation.

Sample 19:

Handspecimen: This is grey coloured ore from Kathpal area. It is a fine grained and very hard ore.

Fig. (4-3): Typical cumulus texture with good amount of silicate matrix between the chromite grains (Reflected light Mag. x 100).

Fig. (4-4): Chromite grains showing pull-apart texture. Fractures filled with silicates (dark coloured) matrix (Reflected light Mag. x 50).

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Polished section (Fig. 4-4): Medium to fine grained with subhedral to euhedral grains of chromite. The ore exhibits pull apart texture. The chromite grains have exsolution lamellae of a phase which has somewhat higher reflectivity. The cementing material is present in large amount between the crystals.

Sample 22:

Handspecimen: This is grey ore with medium to fine grained chromite crystals. It is almost pure chromite ore with very little admixture.

Polished section (Fig. 4-5): Coarse to medium grained chromites, with well developed crystal faces and with lamellae which are bright green in colour. Some cementing material is present between the chromite crystals. The chromite grains, especially the bigger ones show pull-apart texture.

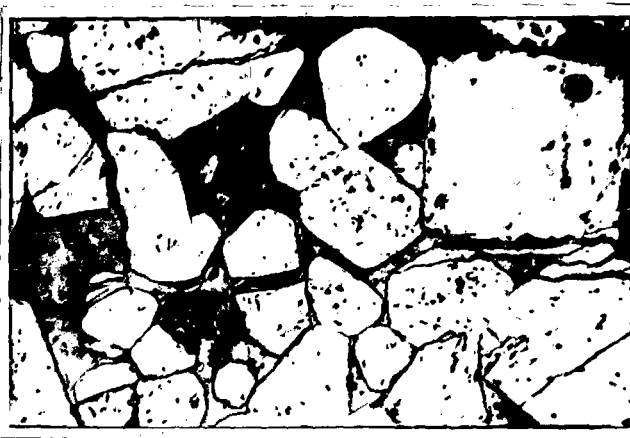
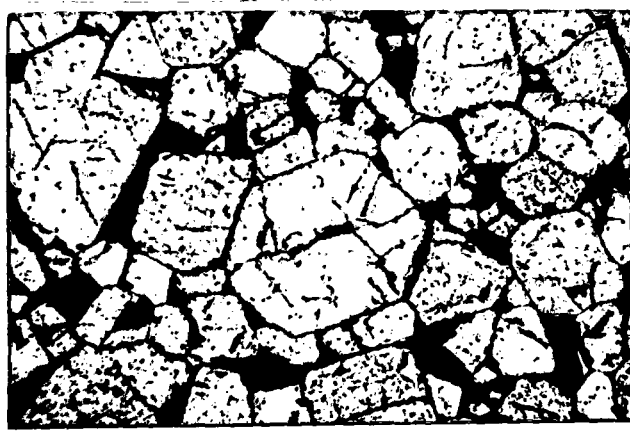
Sample 23:

Handspecimen: This is a banded ore from Kathpal ultramafic body. The banding is very distinct. The chromite is grey coloured and the bands are of serpentine, which appears light greenish in colour.

Polished section (Fig. 4-6): Banding and cumulate texture were observed in this sample. The section shows chromite grains of two different sizes - a larger, euhedral grains with well developed crystalsfaces and a smaller rounded grain.

Fig. (4-5): Larger crystals showing well developed faces and irregular fractures filled with silicates (dark coloured) matrix (Reflected light Mag. x 50).

Fig. (4-6): Chromite ore showing typical cumulus texture. The larger grains have well developed faces and the smaller grains are rounded (Reflected light Mag. x 100).



Sample 35:

Handspecimen: This is grey coloured ore from TISCO grade 1 Quarry. The chromite grains are of coarse to medium size. The ore is well banded with serpentine.

Polished section (Fig. 4-7): The ore is coarse grained with grains having subhedrally developed faces. The grain boundaries are marked by the presence of small amounts of silicate matrix. Some grains exhibit fractures. This is irregularly spotted ore with serpentine and approaches the cumulus texture to some extent.

Sample 37:

Handspecimen: This is greyish ore from Kalarangi Quarry F. The ore is coarse to medium grained, friable ore.

Polished section (Fig. 4-8): This is a massive, coarse grained ore. The chromite grains are in mutual contact without any silicate matrix. Some small crystals are also present between the bigger crystals. The crystals faces are irregular to rounded. Very bright exsolution lamellae are present with developed faces within the chromite grains.

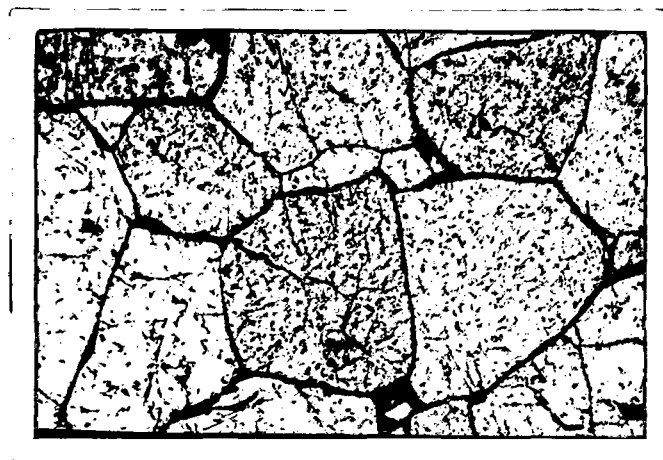
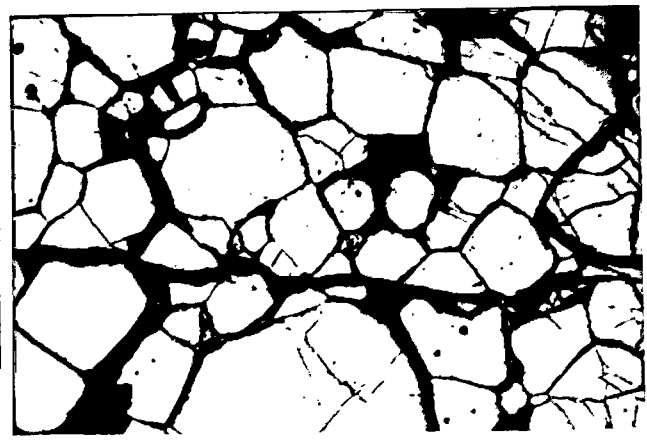
Sample 38:

Handspecimen: This is a very fine grained brown, friable ore from Kalarangi Quarry No. D.

Polished section (Fig. 4-9): The ore is fine grained with some bigger grains which are surrounded by very small grains. Some of

Fig. (4-7): Chromite ore with varying sizes of chromite grains with small amount of silicate matrix (Reflected light Mag. x 50).

Fig. (4-8): Coarse grained massive chromite ore. Chromite grains are in mutual contact without any silicate matrix. Chromite grains showing weakly developed irregular fractures (Reflected light Mag. x 50).



the grains show well developed faces with pull-apart texture in the chromite grains. The chromite grains show bright inclusions. *of what!*

Sample 39:

Handspecimen: This is fine to medium grained spotted ore. The spotted appearance is due to the presence of serpentine clots. The chromite ore is grey in colour and is a hard ore.

Polished section (Fig. 4-10): This section shows the pull-apart texture very clearly. Almost the whole chromite ore is fractured and is filled with serpentine mineral. The silicate matrix is very little in amount. The grains are shattered so badly that the grain outline is difficult to identify, under the microscope.

Sample 44:

Handspecimen: This is coarse grained ore from Saruabil chromite Mines. The ore is greyish in colour and is friable.

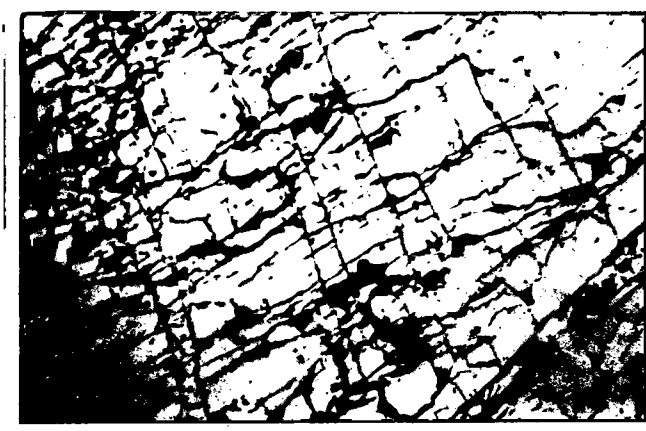
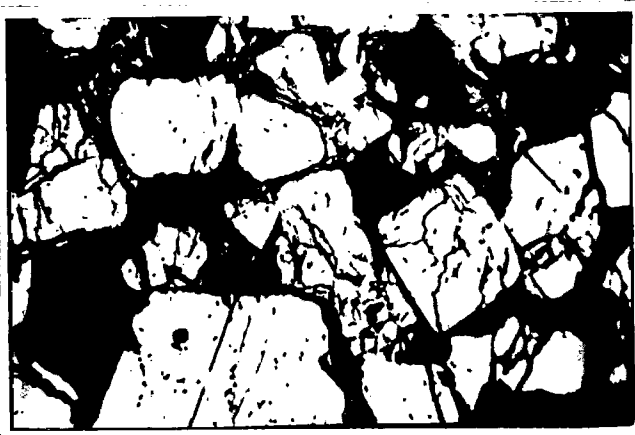
Polished section (Fig. 4-11): Coarse grained ore with well developed faces. The grain boundaries touching each other with very little cement materials. The grains show well developed cleavages. The chromite crystals have inclusions which show irregular faces and are brighter than the chromite crystals.

Sample 47:

Handspecimen: The ore sample is brown coloured from Sarubil chromite Mines. The ore is coarse grained and is very friable.

Fig. (4-9): Chromite ore showing cumulus texture with some well faceted grains showing cleavages and irregular fractures (Reflected light Mag. x 100).

Fig. (4-10): Typical pull-apart texture shown by chromite ore. Chromite grains showing two sets of deformation planes (Reflected light Mag. x 100).



Polished section (Fig. 4-12): The section shows coarse and subhedral grains of chromite, which are in mutual contact. The chromite grains show some regular bright hands.

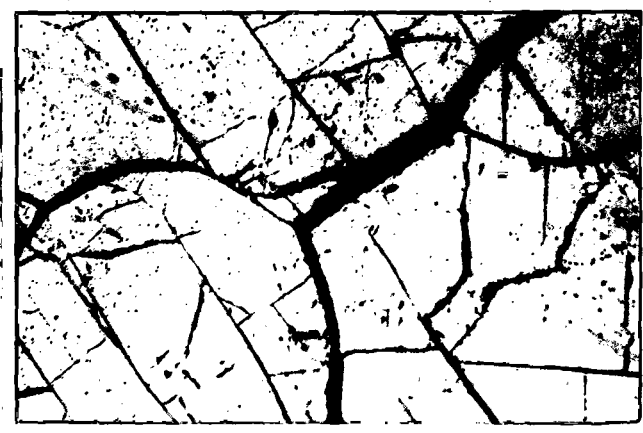
The relationship of the texture with the chromite chemistry and the petrogenesis on the basis of the texture and chemistry will be discussed in Chapter 5.

Emission spectrographic analysis: The spectrographic analysis of the samples were done at the Defence Metallurgical Research Laboratory, Hyderabad, to study the platinum group elements qualitatively.

Principles: When certain metals are introduced as salts into the Bunsen flame, characteristic colours are produced. This procedure has long been used for detecting elements qualitatively. By extending and amplifying the principles inherent in the qualitative flame test, analytical applications of emission spectrography have been developed. Thus more powerful methods of excitation, such as electric spark or electric arc, are used, and the spectra are three kinds of emission spectra: Continuous spectra, band spectra and line spectra. The continuous spectra are emitted by incandescent solids, and sharply defined lines are absent. The band spectra consists of groups of lines that come closer and closer together as they approach a limit, the bands are formed, they are caused by excited molecules. Line spectra consists of definite, usually

Fig. (4-11): Very coarse grained ore. Chromite grains showing well developed cleavages (Reflected light Mag. x 50).

Fig. (4-12): Massive ore with chromite grains showing mutual contact (Reflected light Mag. x 50).



widely and seemingly irregularly spaced lines. These are characteristic of atoms or ions which have been excited and emit their energy in the form of light of definite wave lengths. The lines in the spectra from any element always occur in the same position relative to each other. When sufficient amounts of several elements are present in the source of radiation each emits its characteristic spectrum, this is the basis for qualitative analysis by spectrochemical methods.

Procedure: The chromite samples were mixed with an equal volume of graphite powder. This mixture was taken in a depression, by a pointed counter electrode. For each samples 6 amp DC Arc was employed for 60 seconds. Later the lines recorded on the spectrograph were compared with the standard photographs for the qualitative detection of Pt, Pd, Os, Ir. After comparing these lines, it appeared that, either these elements are below the detection limit or (they are not at all present) in the ore samples, as no sensitive lines for these elements were recorded. Attempts to detect platinum group elements using atomic absorption spectrophotometer at the same laboratory were not successful.

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CHAPTER 5DISCUSSION

In the present study, the discussion on the nature and origin of chromite deposits of Sukinda is based on the published information of the earlier studies and on the present observations. As mentioned before, the two kinds of chromite deposits were distinguished on the basis of their: (1) associated host rocks, (2) mode of occurrences, (3) texture and (4) on their geochemistry.

(1) Associated host rocks: The host rocks for the chromite deposits of Sukinda are typically weathered, extensively silicified and limonitised peridotites. The relict patches of silicate-rich peridotites is almost negligible as compared to the silicified-limonitised masses. No primary mineral except chromite is preserved in this suite of rocks. The original peridotite has been metamorphosed to serpentinites, tremolite-schist, talc-schist, serpentine-talc-schist and chlorite schist. In the middle of the altered ultramafic rocks there is a band of orthopyroxenite which shows little alteration. It appears that this orthopyroxenite is a transitional rock between the peridotite of Sukinda area and gabbroic rock of Bhuban-Godachap area, as has been suggested by Thayer (1960) that the alpine peridotite may grade into gabbro or norites through either of the two intermediate facies, troctolite and olivine-gabbro or pyroxenite. The country rocks show effects of shearing giving rise to cataclastic texture. For example, the

Mahagiri quartzite shows cataclastic texture. Chromites in some ores also show deformation cleavages (Figs. 4-1, 4-10 & 4-11). There is no record of any contact metamorphism on the country rock (Mitra, 1974). There is no clear differentiation pattern shown by the associated ultramafic rocks in terms of their chemistry. These observations suggest that the Sukinda ultramafic complex was probably an alpine type.

(2) Mode of occurrence: The chromite deposits of Sukinda occur in the form of lenses of varying dimensions. For example within the granulite tract, around Maulabhanj Parbat, the chromiferous ultramafites are very small, about 5 to 20 meters in length. Near Bhuasuni Parbat peak the ultramafic body is ovoidal in plan and measures approximately 200 m x 60 m and in them there are 2 to 3 m long and 1 to 2 meters wide layers of chromite (Banerjee, 1972). In Sukinda Khas area the chromite deposits vary widely in shape and persistence, from lenticular masses, measuring 20 m. The grey and massive ore bodies vary in size between 20 x 10 m to 640 x 20 m, the grey and friable bodies vary between 540 x 0.5 to 1 m to 1290 x 9 to 13 m, and the brown ore bodies measure from 80 x 10 m to 930 x 32 m in plan (Banerjee, 1971). Thus the reported mode of occurrence strongly suggests that the Sukinda chromite deposits are similar to podiform chromite deposits which generally occur as tabular or lensoidal bodies with varying sizes.

(3) Textures: Sukinda chromite exhibits two main types of textures. These are typical cumulate texture (Figs. 4-2, 4-3 & 4-6), where chromite crystals are settled in a matrix of silicates, and massive or granular texture (Figs. 4-1, 4-8, 4-10, 4-11 & 4-12). A third variety of texture is between the massive and cumulate texture but with well developed crystal faces (Figs. 4-4, 4-5, 4-7 & 4-9). We get typical pull-apart texture in the massive or granular ore as shown in Figures (4-10 & 4-1) and in the well crystallised samples (Figs. 4-9, 4-5 & 4-4). In the cumulate texture we get both euhedral and rounded grains with silicate minerals forming the matrix. In the massive ore the samples are very coarse grained and the matrix is very small in amount between the crystal boundaries. Thus in their textural characteristics also Sukinda chromite deposits are similar to Podiform chromites which are typically associated with alpine-type ultramafic bodies.

(4) Geochemistry: In order to understand the geochemical nature of Sukinda chromites, the present chemical data as well as those of Banerjee's (1972) are discussed here in the light of recent developments in the geochemistry of chromite deposits. Figure (5-1) shows that all the chromite analyses from Sukinda area are restricted to the aluminian chromite region of Steven's classification of the spinel group (Steven's, 1946). Podiform chromites

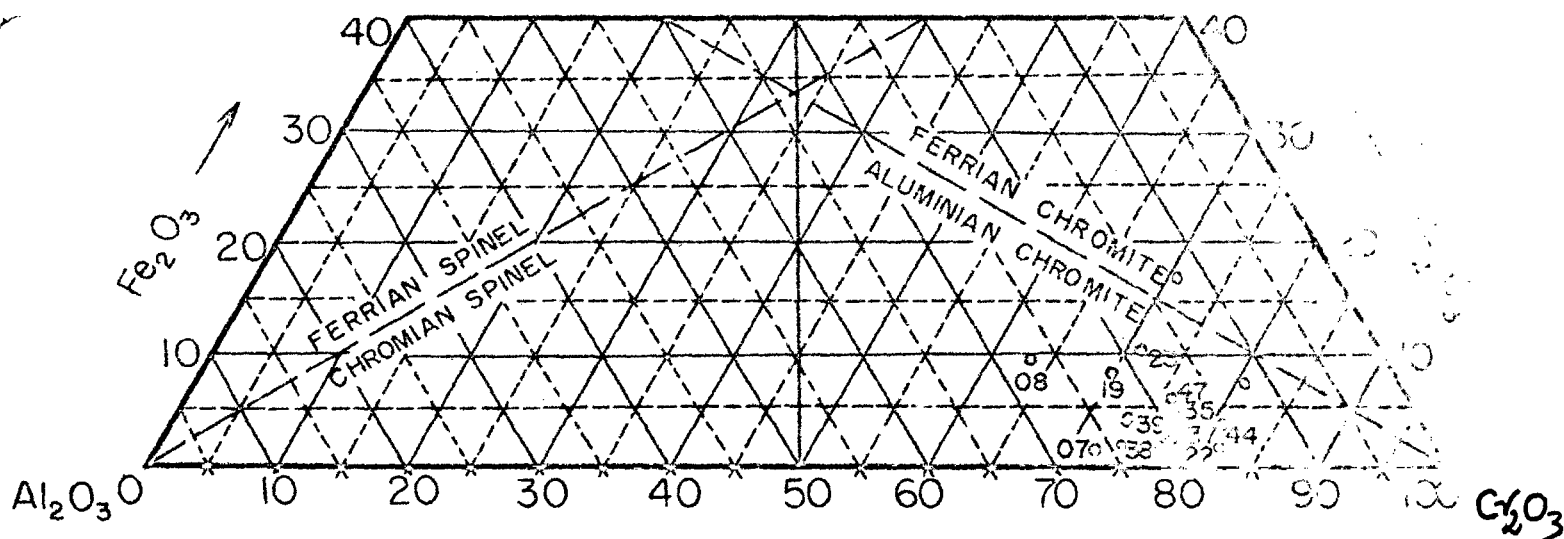


Fig. (5-1): Variation of Cr_2O_3 , Al_2O_3 and Fe_2O_3 (in mol. per cent of total R_2O_3) in chromite ore samples from Sukinda. Black dots = Present study and Orange dots = Banerjee's (1972) data.

are generally believed to be aluminian chromites in terms of their R_2O_3 distribution, whereas the stratiform chromite plots in the region of aluminian chromite, ferrian chromite, chromian spinel and ferrian spinel regions of the Steven's spinel group classification diagram (Thayer, 1964). All the samples are very poor in Fe_2O_3 (5 mol. % in total R_2O_3) around 78 mol. % of Cr_2O_3 and 20 mol. % of Al_2O_3 of the total R_2O_3 . Thayer reported that in podiform chromite deposits, Cr_2O_3 content varies between 70 and 80 mol. %, Al_2O_3 between 15 and 25 mol. % and Fe_2O_3 between 5 and 8 mol. % of the total R_2O_3 (Thayer, 1964). Chemical analyses reported by Banerjee (1972) for the Sukinda chromite from different part of the ultramafic complex have also been plotted in the same figure which indicates the present data agree with those of Banerjee's. Thus on the basis of R_2O_3 distribution, it is suggested that the Sukinda chromite deposit is an alpine type of chromite or a podiform type of chromite deposit. The analyses are also plotted on the $Cr:Al:Fe^{3+}$ diagram (Fig. 5-2), proposed by Dickey (1975). Sukinda chromites are again similar to podiform chromite associated with alpine type ultramafics/opiolite complex reported by Dickey & Greenbaum (Dickey, 1975; Greenbaum, 1972 and 1977). Figure (5-2) also indicates that there appears to be an inverse relationship between Cr^{3+} and Fe^{3+} . The variation diagram $Cr \times 100 / Cr + Al$ vs $Mg \times 100 / Mg + Fe^{2+}$ (Fig. 5-3) shows that the samples are very

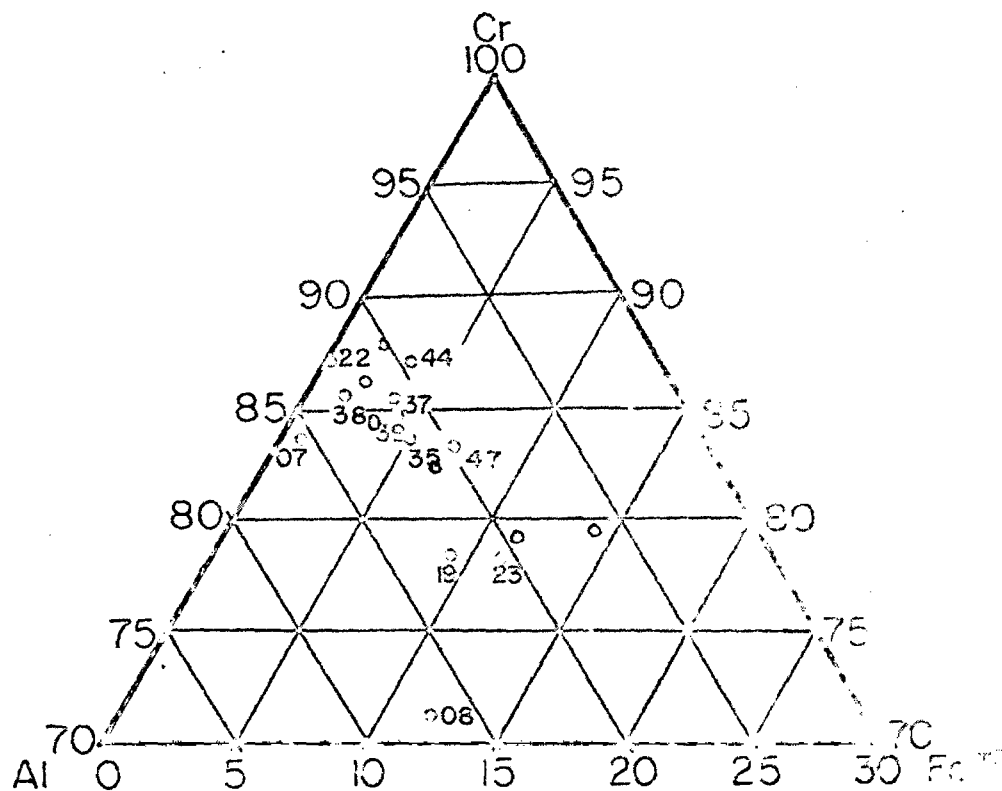


Fig. (5-2): Variation in $\text{Fe}^{3+}:\text{Cr}:\text{Al}$ in chromite samples from Sukinda. Black dots = Present study and Orange dots = Banerjee's (1972) data.

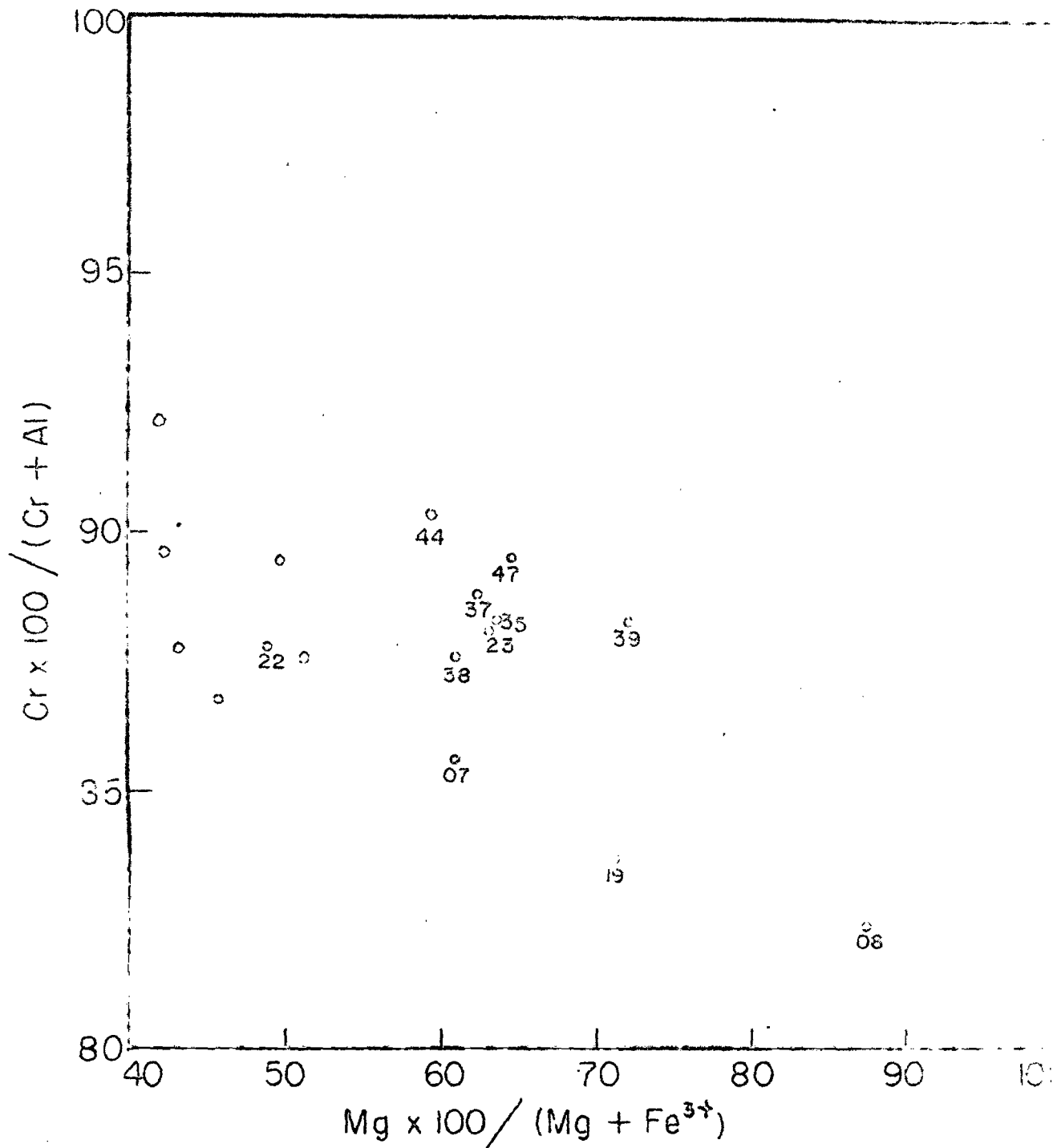


Fig. (5-3): Variation in $Cr \times 100 / (Cr + Al)$ vs $Mg \times 100 / (Mg + Fe^{2+})$ in chromite samples from Sukinda. Black dots = Present study and Orange dots = Banerjee's (1972) data.

rich in Cr and Mg contents. The chromite from podiform deposits are typically rich in Mg content (Dickey, 1975). The ratio of $\text{Mg}:\text{Fe}^{2+}$ is relatively constant for all the chromite samples. This relatively constant $\text{Mg}:\text{Fe}^{2+}$ ratio are characteristic of alpine peridotite (Dickey, 1975, Malpas and Strong, 1975). However, the $\text{Mg}:\text{Fe}^{2+}$ ratio is believed to be quite variable in chromite deposits associated ^{with} large layered intrusions (Irvine & Findley, 1972, Dickey, 1975 and Thayer, 1974). The Cr:Al ratios of Sukinda chromite are also similar to podiform chromite reported by Irvine (1967). Thus in all these aspects discussed above Sukinda chromites resemble several podiform chromites from different ophiolite complexes like the Bay of Islands, the Gander River Belt and Burlington Peninsular reported by Malpas and Strong (Malpas and Strong, 1975).

The variation diagram for $\text{Fe}^{3+} \times 100 / \text{Cr} + \text{Al} + \text{Fe}^{3+}$ vs $\text{Mg} \times 100 / \text{Mg} + \text{Fe}^{2+}$, Fig. (5-4) shows that the samples are generally very low in Fe^{3+} content. These plots agree with values of Limassol Forest Chromite, reported by Panayiotou (Panayiotou, 1978), which in turn is comparable to the podiform chromite of Troodos -massif reported by Greenbaum (1977). The Sukinda chromite and Limassol Forest Chromite are slightly higher in $\text{Fe}^{3+} \times 100 / \text{Cr} + \text{Al} + \text{Fe}^{3+}$ ratio than the Troodos chromite values. This higher value of Fe^{3+} may be attributed either to high oxygen fugacity

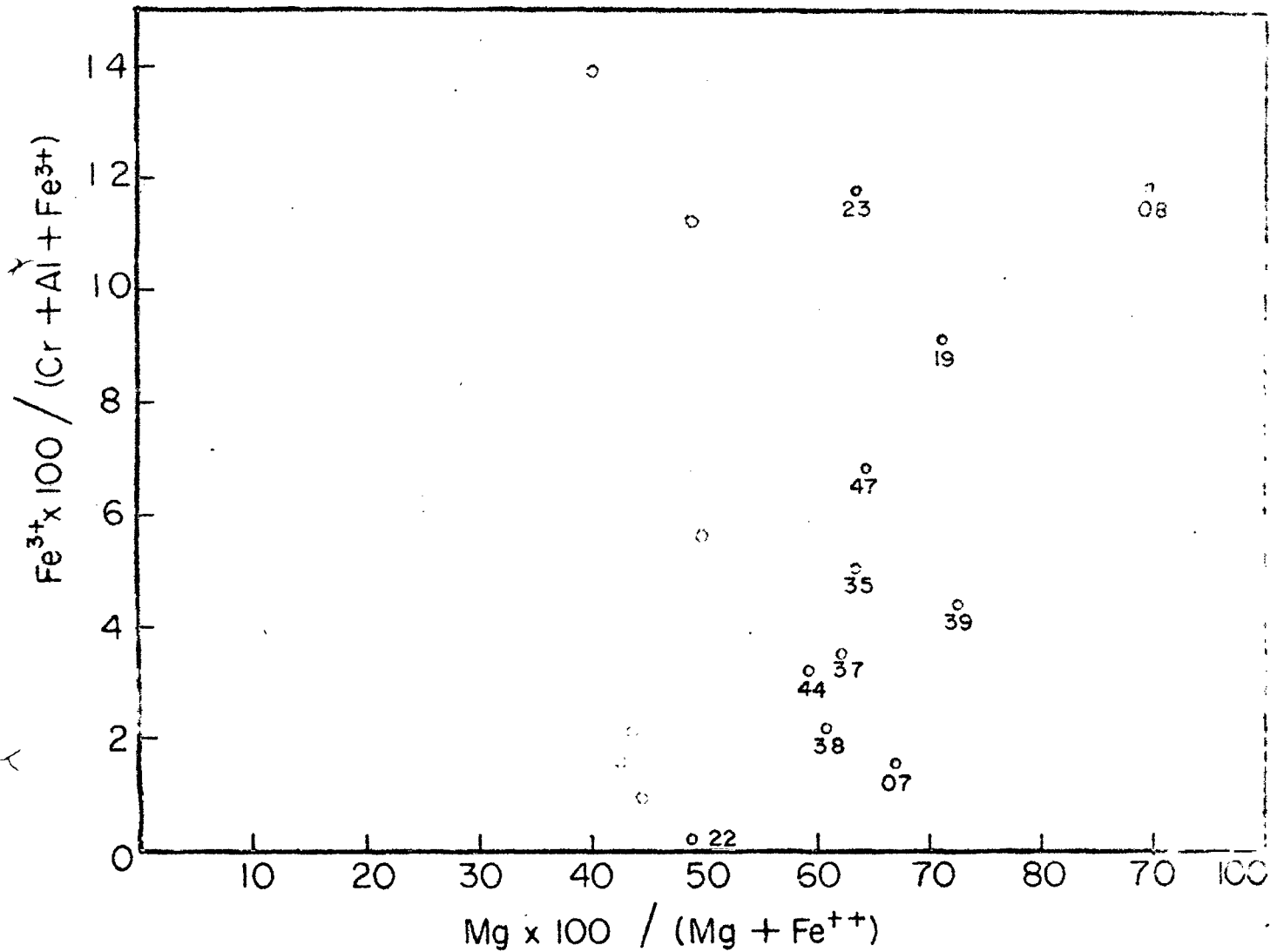


Fig. (5-4): Variation of $\text{Fe}^{3+} \times 100 / (\text{Cr} + \text{Al} + \text{Fe}^{3+})$ vs $\text{Mg} \times 100 / (\text{Mg} + \text{Fe}^{2+})$ in chromite samples from Sukinda. Black dots = Present study and Orange dots = Banerjee's (1972) data.

during the crystallisation of chromites or to the secondary oxidation during serpentinisation. It is noted here that Figure (5-4) indicates that the observed Mg values in the present study are higher than those reported by Banerjee (1972). Also there appears to be a positive relationship between Fe^{3+} and Mg^{2+} contents of chromites of Sukinda. This relationship can be explained by the fact that with increasing oxygen fugacity, the amount of magnesio-ferrite (MgFe_2O_4) molecule in the spinel group increases, as pointed by Thayer, (1946) and Osborn (1959). The fact that there exists a positive relationship between Fe^{3+} and Mg^{2+} in chromites is confirmed by Figure (5-5), where Fe^{3+} shows a reciprocal relationship to Fe^{2+} . From the variation diagram for Cr_2O_3 in total R_2O_3 vs MgO in total R_2O_3 , Figure (5-6), there is very clear reciprocal relationship between the Cr_2O_3 and MgO content and the MgO content increases with the increasing Fe_2O_3 in R_2O_3 (Fig. 5-7). The Cr:Fe ratio for all samples are $> 4:1$. This is in accordance with the ratio observed by Thayer (1960) for alpine type chromite where, he suggested, Cr:Fe ratio to be not less than 2:1, but can exceed 4:1 ratio. For stratiform deposits, however, this ratio averages between 1.5 and 1. The FeO:RO ratio is around 20 mol. % which is again confirming with alpine type values whereas for the stratiform chromite the FeO:RO ratio according to Thayer, averages to about

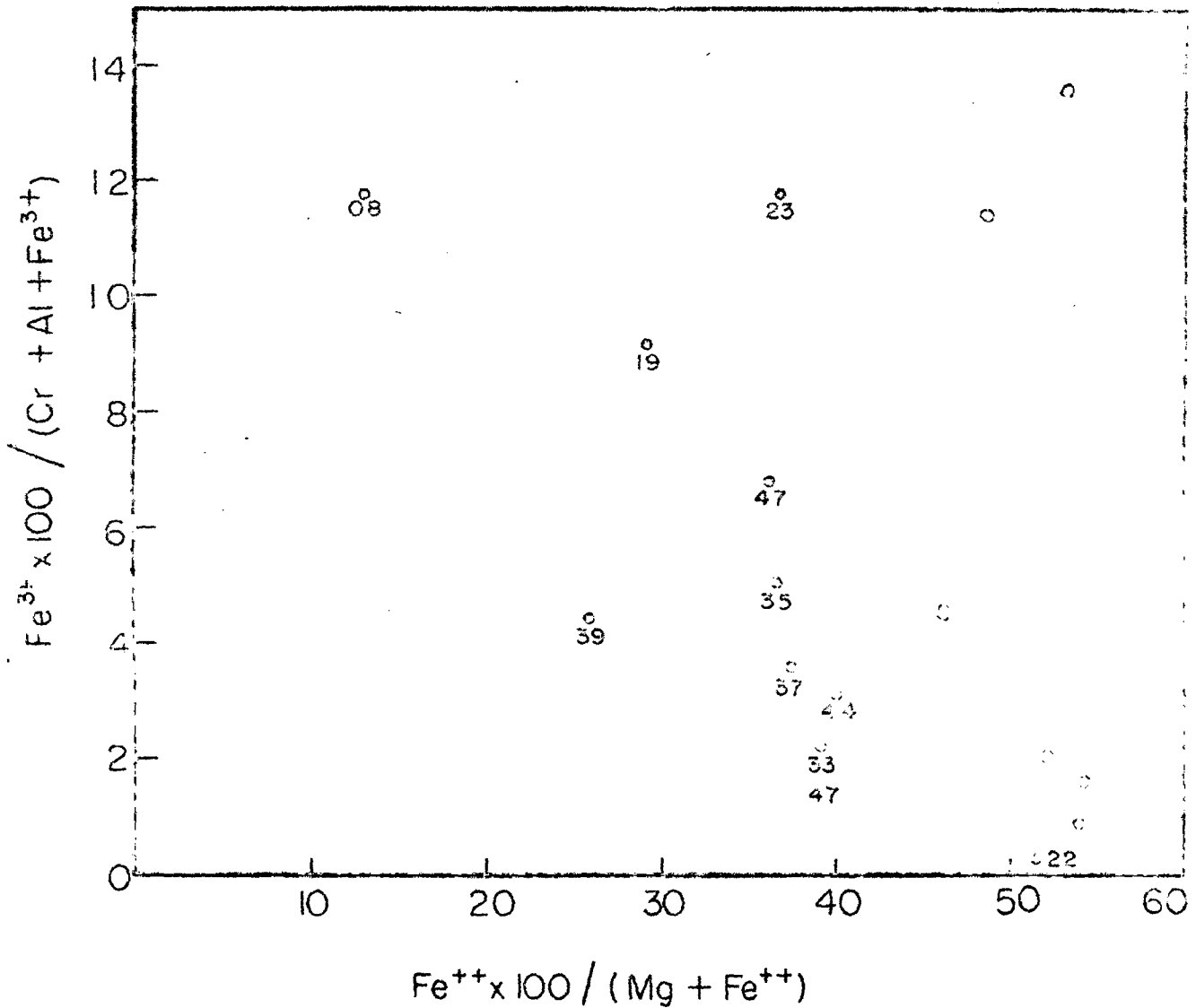


Fig. (5-5): Variation of $\text{Fe}^{3+} \times 100 / (\text{Cr} + \text{Al} + \text{Fe}^{3+})$ vs $\text{Fe}^{2+} \times 100 / (\text{Mg} + \text{Fe}^{2+})$ in the chromite samples from Sukinda. Black dots = Present study and Orange dots = Banerjee's (1972) data.

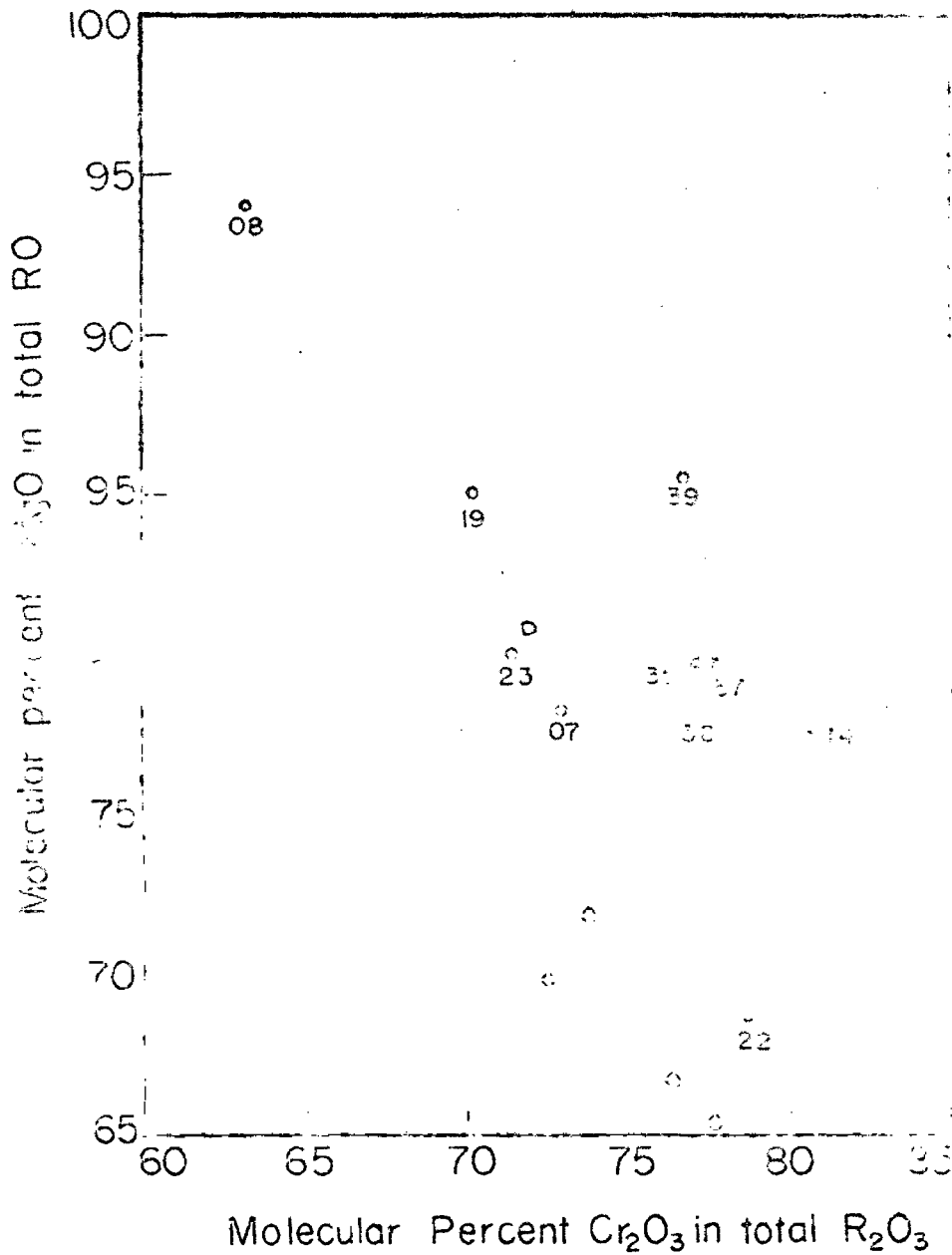


Fig. (5-6): Variation in molecular percentage MgO in total RO vs molecular percentage Cr_2O_3 in total R_2O_3 in chromite samples from Sukinda. Black dots = Present study and Orange dots = Banerjee's (1972) data.

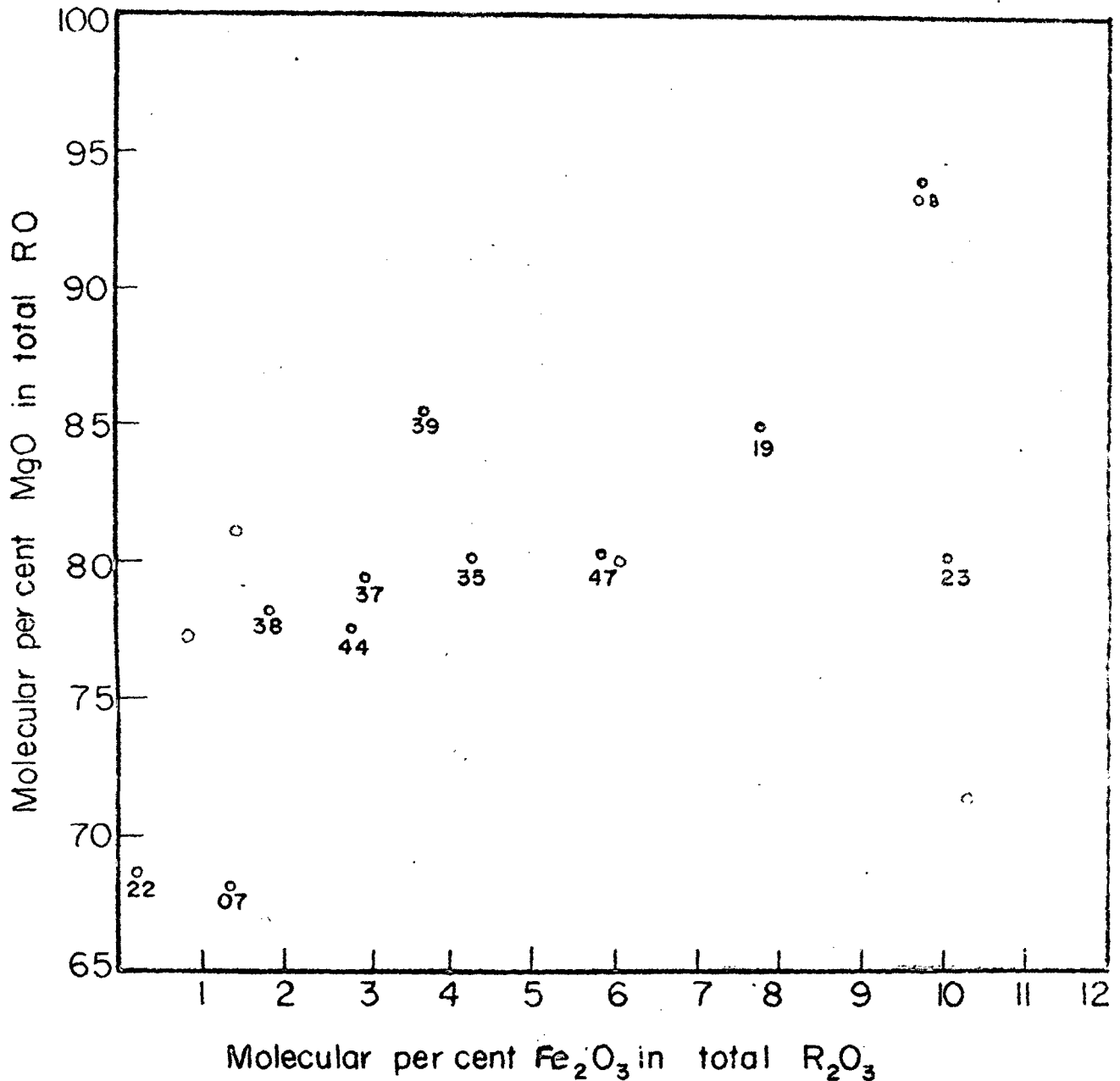


Fig. (5-7): Variation in the molecular percentage of MgO in total RO vs molecular percentage of Fe₂O₃ in total R₂O₃ in the chromite samples from Sukinda. Black dots = Present study and Orange dots = Banerjee's (1972) data.

50-55 mol. % (Thayer, 1960). There is no relationship between the texture of the ore and its chemical composition in terms of any of the oxides. This irregularity in composition is another characteristic feature of the chromite ores of alpine type association. The accessory chromites are associated with serpentinites and other hydrothermally altered silicate rocks and also with unaltered orthopyroxenite. All these accessory chromites are very rich in Fe content. For example, Banerjee observed that the composition of the accessory chromite is $(\text{Mg}_{30}\text{Fe}_{70}) (\text{Cr}_{72}\text{Al}_{28})$ whereas in the ore chromites from the same host rock, the Fe^{2+} content varies only between 19 and 38. The accessory chromite associated with orthopyroxenite has the formula composition of $(\text{Mg}_{41}\text{Fe}_{59}) (\text{Cr}_{76}\text{Al}_{21}\text{Fe}_3)$ (Banerjee, 1972). It is suggested here that the higher Fe^{2+} content of accessory chromite is mainly due to subsolidus reequilibration of chromites with the ferromagnesian silicates, which causes an increase in the Fe^{2+} content of chromite without noticeable change in Mg:Fe ratios of the silicates. It is also possible, particularly in the accessory chromite associated with orthopyroxenite that the higher iron content could be due to later crystallisation of chromite from a fractionated, Cr depleted magma. Banerjee has reported a systematic variation in MgO:FeO ratio from the lowest to the highest ore levels. The trend of variation is fairly steady, and ranges between 1.48 to 2.36 at the lowest grey and massive ore and 1 at

the upper most brown ore levels (Banerjee, 1972). Unfortunately sample locations were not indicated in the previous study. But no such systematic variation was seen in the present study. Variations in other oxides and their ratios were not found to be regular. This erratic variation in chemical composition again indicates the podiform nature of Sukinda chromites.

Thus all the four lines of evidences suggest that the Sukinda ultramafic body and their associated chromite ore could be of alpine type, rather than a stratiform type.

It is interesting to discuss here the mechanism by which the podiform chromites are formed, as suggested by Dickey (1975). This requires the partial melting of the mantle lithosphere at depth and the production of a tholeiitic melt and refractory residuum (harzburgite). Bird and Isaacks, in their plate tectonics theory, suggested partial melting of the mantle beneath ocean ridges or rises along the boundaries between diverging plates (Bird and Isaacks, 1972). As the lithospheric plates separates, mantle material of peridotite composition rises from the asthenosphere to a level where anatexis (partial melting) produces a silicate melt of tholeiitic composition and residual solids (harzburgite). According to Kushiro, at depths of 15 to 25 km much of the liquid is segregated into bodies that are large enough to fractionate and generate significant volumes of basaltic magma (Kushiro, 1973). The tholeiitic magma may emerge as pillow lavas

on the sea floor, may freeze as steeply dipping dikes in the rift zone that feed the lavas or they may form pockets of magma that fractionate between the sheeted dikes and the harzburgite. As this separation continues, the unmelted, residual materials is moved laterally off the zone of partial melting and magma segregation. The effect of this lateral displacement is analogous to the industrial process of "zone refining", where an impure material is passed through a zone of partial melting. The constituents with low temperature of melting are retained and are enriched, more refractory constituent passes beyond this zone. So an exceedingly clean separation is achieved between the low melting constituents and the residual solid. The magma pockets may give rise to massive chromite concentration, and deposits with fine cumulus texture are formed. Dickey suggested that these deposits are long and narrow because they form along the plate margins. These chromite-rich cumulates sink or descend, as podiform autoliths, into the residual tectonite peridotite because of their higher density.

Finally, the emission spectrographic and atomic absorption spectrophotometric studies suggested that platinum group elements could be present only below 1 ppm level in the chromite deposits of Sukinda. A detailed investigation on this aspect has been planned for the future.

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