

SEQUENCE OF CHROMITE CRYSTALLIZATION AT BOULA - NAUSAHI IGNEOUS COMPLEX, ORISSA, INDIA

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ABSTRACT

The chromite deposit at Boula-Nausahi Igneous Complex is of stratiform type where chromite occurs as layers in ultramafic rocks. The chromites in this complex can be ascribed to early and late stage crystallization based on differences in their physical, chemical and beneficiation characteristics. The early stage chromites are characterised by their association with serpentinite, coarser grain size, nonmagnetic nature, high Cr content, high Cr/Cr+Al ratio, average chemical composition (Cr₂O₃-51.9%, FeO-26.9%, MgO-10.3%, Al₂O₃-10.2%, TiO₂-0.45%, V₂O₅-.2%, Cr/Fe-1.74) and amenability to simple beneficiation techniques. On the contrary, the late stage chromites are characterised by their association with fine grained fibrous and magnetic silicates, fine grain size, magnetic behaviour, low Cr content, low Cr/Cr+Al ratio, average chemical composition (Cr₂O₃-27%, FeO-53.7%, MgO-6%, Al₂O₃-10.5%, TiO₂-2.5, V₂O₅-0.4% and Cr/Fe-0.45) and difficult to beneficiation.

Key words: chromite, crystallization, Boula-Nausahi igneous complex, Orissa.

INTRODUCTION

Chromite deposits of Pre Cambrian (Iron Ore Group and Eastern Ghats) and Tertiary age are distributed in shield and tectonically mobile areas in India. Out of the 11 major chromite deposits distributed in 9 states of India, Orissa hosts the largest chromite reserve of the country and also produces the lion share of total Indian production. In Orissa, the two major deposits i. e. Sukinda Ultramafic Belt and Boula Nausahi Igneous Complex hold around 98% of the total Indian reserve. Boula-Nausahi Igneous complex (21°18'-21°15' N; 86°18'-86°20'E) consists of three rock units i e., the ultramafic rocks, mafic rocks and the felsic rocks. The ultramafic body, which hosts four chromite lodes, occurs as a dyke like pluton of 3 km long and 0.6 km width at the central part. Besides chromite, the ultramafic-mafic rocks host PGE mineralisation along with sulphides (Cu-Ni-Fe-Ag). Mining activity in this area is going on since 1942 for chromite. Though most of the workers are in favour of a magmatic origin for the chromite and the associated rock types in this complex, opinions are divided on the stage(s) of chromite crystallization as to whether they are early magmatic (Barooah, 1948; Ghosh, Prasad Rao, 1952; Mukherjee, 1962) or late magmatic (Chakraborty, 1958).

An attempt has been made in this paper to find out the stages of chromite crystallization based on the physical, mineralogical, chemical and beneficiation characteristics of chromites.

GEOLOGY

The mafic-ultramafic suit with chromite and Ti-V magnetite of early Proterozoic age is well exposed in the southeastern periphery of the Singhbhum Granitic batholith. Many plutons are emplaced into the cratonic

nucleus comprising Singhbhum Granite, Iron Ore Group and the Early Proterozoic supracrustal rocks. Boula-Nausahi complex is situated on the girdle of Sukinda-Nilgiri shear zone that extends discontinuously from Nilgiri in the east through Boula-Nausahi upto Sukinda in the west. The chromiferous ultramafic rocks have been emplaced within the interbanded sequence of quartzite, chert, quartz-mica schist of Iron Ore Group (Fig. 1). Age of emplacement of this complex is between 2000 – 2100 Ma (Saha, 1994). The ultramafic rocks occur as elongated pluton with tapered ends and extends in a NNW-SSE direction with moderate dip towards east. They host 4 layers of chromitite ore bodies of varying thickness. They are Durga, Laxmi, Sankar and Ganga arranged from bottom to top in a northerly direction. These four ore bodies alternate with ultramafic (± mafic) rocks exhibit layering typical of stratiform igneous complexes.

PETROGRAPHY

The ultramafic rocks are represented by dunite-peridotite, websterite, lherzolite and enstatitite. Olivine is the major mineral followed by orthopyroxene. Detail mineralogical and chemical studies of the rock types and the associated chromite ore bodies have been carried out by Mohanty (1994). The salient features are as follows:

The chromiferous ultramafic rocks exhibit magmatosedimentary structures/ textures such as cumulus, rhythmic and cryptic layering, graded bedding (grain size variation), current bedding and cusp etc. The chromitites exhibit primary (cumulus, chain syneusis, clot, exsolution, foam), deformational (brecciation, mylonitisation, pull-apart) and alteration (zoning) textures. The four layers exhibit size grading from coarse at bottom to fine at top. A log normal straight line size distribution indicates uninterrupted

chromite crystallization. Unimodal size distribution of chromite and predominance of coarse grains of chromite in layers from bottom to top indicate continuous crystallization in quiet - plutonic condition from a single source. Gravity settling of the chromite crystals under steady state condition is responsible for the formation of chromitite layers. The rocks and the ore bodies are co-magmatic in nature. They are derived from a low K-tholeiitic magma in a decreasing temperature and increasing oxygen fugacity condition.

CHROMITE

Chromite mostly consists of chromite with subordinate amounts of ferritchromite, magnetite, ilmenite and secondary silicates like serpentine, talc, tremolite, uvarovite and kammererite. Though the chromite grains are predominantly euhedral in nature, they exhibit two fold variations in physical, mineralogical and chemical characters which can be correlated with their formation at different stages during crystallization process. In this complex, chromites have crystallized in two stages. The chromites from two stages differ in these following aspects.

Mineralogical and physical characters

The chromites of two stages exhibit variations in physical properties, optical characters and mineralogy.

The chromite grains exhibit a variation in reflectivity from 12.5 to 16.2%. The reflectivity measurement data indicates two clusters around 13% and 16%. The chromites which exhibit reflectivity around 16 may represent late stage crystallization. The low reflectivity cluster indicates early stage chromite crystallization. Chromites with higher reflectivity may be due to higher trivalent iron content (Eales, 1980).

The chromite grains contain inclusions of various shape, size and composition. The inclusions in early stage chromites are mostly olivine and enstatite (now altered to serpentine) and in late stages they are mostly diopside, amphibole, muscovite etc.

The two stage chromites have different magnetic character. The early stage chromites are non-magnetic with a very low magnetic susceptibility (3.4×10^{-5} emu/gm.Oe) compared to the late stage ores which are highly

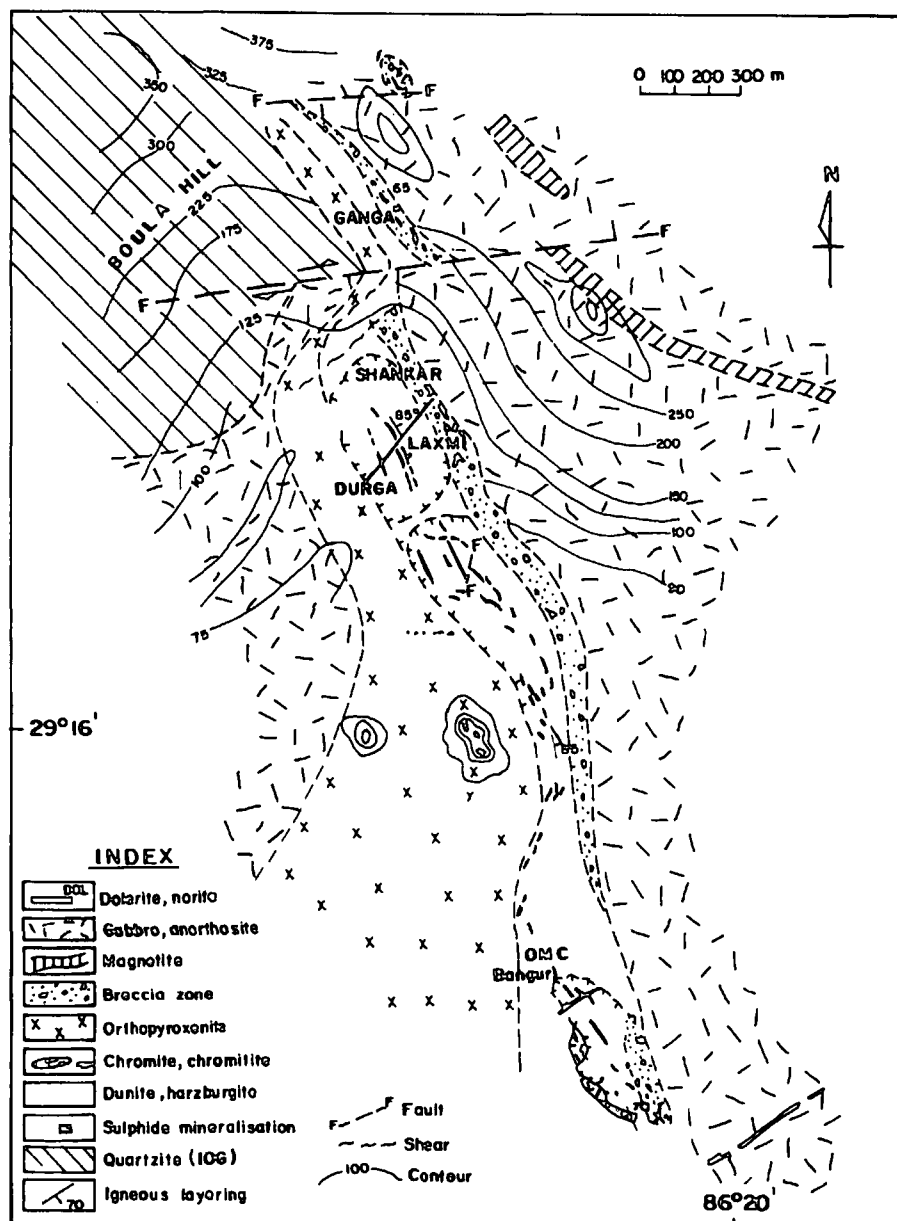


Fig. 1. Geological map of Boula-Nuasahi Igneous Complex, Keonjhar District, Orissa.

magnetic with high magnetic susceptibility (0.11 emu/gm. Oe). Mossbauer study of the chromite samples indicates that the early and late stage chromites exhibit spectral differences. While the early stage chromites exhibit normal spinel spectra, the late stage chromites exhibit two magnetically split narrow sextets. They also exhibit superposition of magnetically ordered, paramagnetic and super paramagnetic components.

Besides magnetic behaviour, the chromites also exhibit variation in their cell dimension. The early formed chromites have cell dimension around 8.28\AA where as the late formed chromites almost approach the cell dimension of magnetite (8.37\AA). The variation in magnetic character and cell

dimension of chromites may be due to increase in trivalent iron content.

The alteration characters of the two types also vary in a sense that the early formed chromites which are generally associated with olivine alter to magnetite along with the silicate mostly altered to serpentine. The late stage chromites which are associated with pyroxene alter to ferritchromite + magnetite association with associated silicates mostly altering to talc and sometimes to chlorite.

The late stage chromites contain ilmenite granules and exsolution lamellae where as the early formed chromites are devoid of it. Presence of ilmenite in late stage chromites indicates their crystallization from Fe-Ti rich Cr poor magma.

Sulphide minerals are ubiquitous in ultramafics. In this complex both primary and secondary sulphide minerals are present through out the ultramafic belt. The late formed chromites contain primary sulphide minerals (pentlandite, chalcopyrite, pyrrhotite etc.) as inclusions where as the early formed chromites devoid of any primary sulphide minerals. However secondary sulphide minerals are present in both early and late stage chromites.

Broadly speaking the mineralogical assemblage of the two stages of chromite mineralisation can be expressed as chromite (+magnetite) + sulphide (secondary) + serpentine for the early stage and chromite (+ ferritchromite + magnetite) + Sulphide (primary + secondary)+ ilmenite + talc + tremolite + chlorite for the late stage chromites.

Chemical characters

To know the compositional variations in the chromites of two stages, massive fresh chromite samples were collected from the four ore bodies and the concentrates were analysed by wet chemical methods. The data are presented in Table 1. From the Table 1, it is observed that the early chrome spinels are rich in Cr_2O_3 content which varies from 41% to 59.5%. Cr/Fe ratio varies between 2.7 to 1. Al_2O_3 content varies from 5 to 14%. The variations of FeO(t), MgO, TiO_2 and V_2O_5 are 22% to 39%, 6.7% to 12.5%, 0.26 to 0.76% and 0.1 to 0.3% respectively. Comparatively late chromites are characterised by low Cr_2O_3 (21.5 to 36%), high FeO (48 to 58%), high TiO_2 (1.8-2.7%) and low Cr/Fe ratio (<1). When the composition data are plotted in Stevens' classification diagram (1944), the chromites belong to aluminian field with a minor distribution in chromian magnetite and ferrian chromite fields (Fig. 2). The chromites also exhibit compositional variation from Cr corner towards (Fe + 2Ti) corner in Cr-Al- (Fe+2Ti) diagram of Eales (1980). From the distribution of chromite in these diagrams two stages of chromite crystallization is clearly revealed. The two stages of crystallization seems to be a continuous one and the stages are assigned early stage giving rise to normal chromite spinel and late stage

Table 1. Chemical analysis of chromites from different ore bodies of Boula Nausahi igneous complex (wt%)

Sl.No	Ore body	Cr_2O_3	FeO	MgO	Al_2O_3	TiO_2	V_2O_5	Total
1	DURGA	59.48	22.01	12.56	5.27	0.37	0.1	99.79
2		57.72	22.61	12	6.65	0.53	0.12	99.63
3		54.91	23.71	11.64	9.82	0.27	0.1	100.45
4		55.21	23.24	12	9.24	0.3	0.11	100.1
5		55.32	23.4	11.84	9.12	0.26	0.1	100.04
6	LAXMI	54.21	24.53	10.34	9.37	0.38	0.16	99.01
7		53.42	26	9.8	10.2	0.38	0.2	100
8		52.64	26.72	9.26	10.78	0.45	0.22	100.07
9		52.81	25.65	10.5	9.8	0.3	0.1	99.16
10		52.65	25.80	10.34	9.95	0.28	0.2	99.22
11		52.55	26	10.2	10	0.33	0.21	99.28
12		52.12	28.04	9.43	9.84	0.35	0.21	100.08
13		51.32	25.36	8.95	11.87	0.53	0.24	98.27
14		52.26	25.84	9.62	11.35	0.57	0.25	99.89
15		51.45	28.56	9.65	8.75	0.45	0.21	99.07
16		51.63	27.15	10.33	9.25	0.6	0.22	99.18
17		52.38	27.18	10.83	9.84	0.35	0.19	100.77
18		51.63	25.59	10.34	11.44	0.27	0.18	99.45
19		51.54	26.52	10.85	10.15	0.42	0.22	99.7
20		49.96	28.46	10.54	10.21	0.56	0.21	99.94
21	SHANKAR	49.48	26.08	8.89	14.4	0.62	0.25	99.72
22		49.91	27	8.65	13.86	0.74	0.30	100.46
23		47.32	32.06	6.85	12.9	0.76	0.34	100.23
24		44.65	35.75	9.18	10.2	0.41	0.15	100.34
25		40.78	39.02	8.78	11.23	0.73	0.11	100.65
26	GANGA	35.83	48.02	7.83	6.48	1.77	0.3	100.23
27		29.05	50.52	6	11.57	2.67	0.33	100.14
28		25.51	54.91	5.8	11.36	2.63	0.42	100.63
29		23.07	57	5.3	10.78	2.63	0.41	99.19
30		21.57	57.81	5.12	12.35	2.73	0.35	99.63

(Sl.No. 1-25: Early stage chromite; Sl.No. 26-30: Late stage chromite)

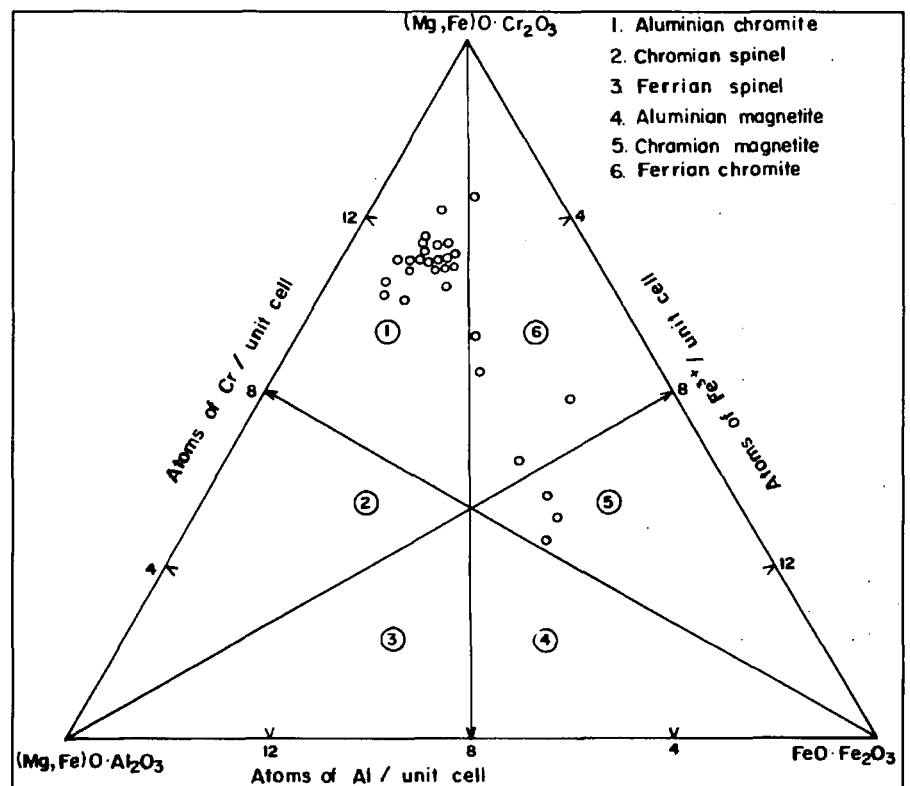
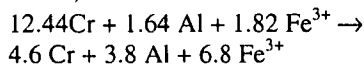


Fig. 2. Classification of chromites of Boula-Nuasahi Igneous Complex (after Stevens, 1944).

giving rise to iron rich chromite spinel. The two types of chromites show distinct chemical differences averages of which are clearly reflected in Table 1. The compositional variation in entire gamut of chromites of this complex is graphically represented in Fig. 3.

Depending upon the composition of the parent magma, concentration of Cr, temperature and oxygen fugacity, chromite crystallizes independently or in association with olivine or orthopyroxene. In this complex, chromite is predominantly associated with olivine and orthopyroxene. However the late stage chromites are associated with orthopyroxene and clinopyroxene which are now altered to talc, tremolite. Depending upon the temperature of crystallization and concentration of different elements, cationic substitution takes place in the chromite structure and it is reflected in the chemical composition of the chromites. The chemical composition of clean chromites indicates that Cr content in the unit cell decreases from 12.44 in the early formed chromite to 4.6 in the late formed chromites. Likewise other cations also exhibit similar variation in the chromites. Typical cationic distribution in chromites from two stages is given below;



(Early stage \rightarrow Late stage)

This cation distribution indicates that Cr content of the early stage chromites are being substituted by both Al and Fe^{3+} in the late stage chromites. Similarly Mg is substituted by Fe^{2+} at the tetrahedral site in the late stage chromites (Fig. 4).

When these chromites are plotted in Y_{Cr} and $Y_{\text{Fe}^{3+}}$ vs. MMF diagram, two stages of chromite crystallization is clearly observed. Chromites with higher Y_{Cr} , $\text{Cr}/\text{Cr}+\text{Al}$ and Cr/Fe ratio represent the early stage whereas the chromites with high $Y_{\text{Fe}^{3+}}$ and low Cr/Fe ratio indicate late stage of crystallization. The early formed chromites have high Y_{Cr} , Cr cation >10 and $\text{Cr}/\text{Cr}+\text{Al}$ ratio whereas the late stage chromites are low in Y_{Cr} , Cr cation <10 and low $\text{Cr}/\text{Cr}+\text{Al}$. Higher $\text{Cr}/\text{Cr}+\text{Al}$ ratio of the early formed chromites indicate a higher temperature of crystallization (Irvine, 1967).

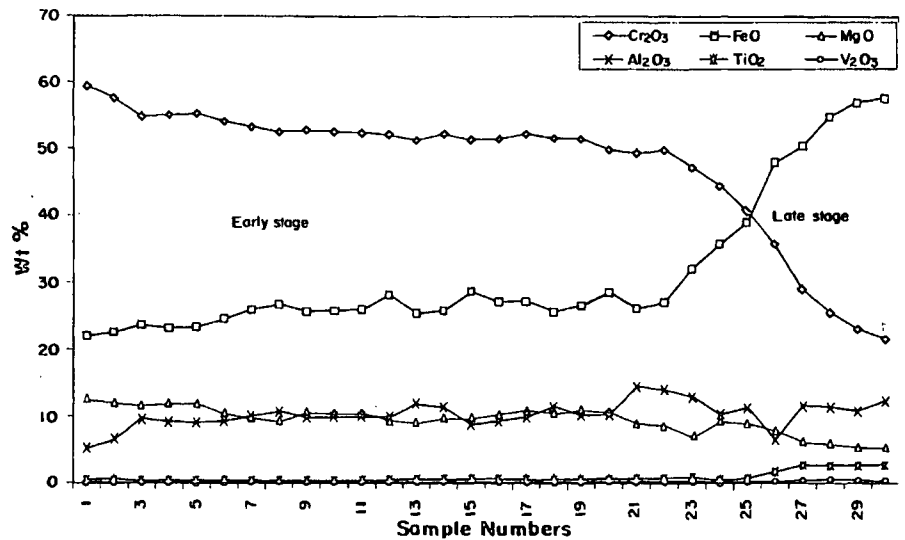


Fig. 3. Compositional variations in chromites of Boula-Nuasahi Igneous Complex.

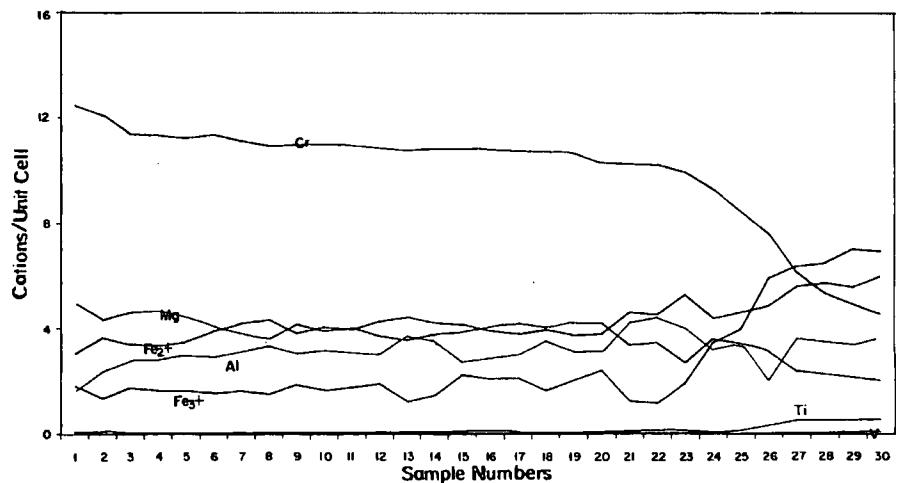


Fig. 4. Cation distribution in chromites of Boula-Nuasahi Igneous Complex.

Olivine associated with early chromite is Mg rich. From the trivalent iron content in the chromites it is observed that the early stage chromites are formed at a lower f_{O_2} than the late stage chromites (Murck, Campbell, 1986). Owing to a relative increase in the iron content during late stage, some of Fe^{2+} were oxidised to Fe^{3+} and entered into the octahedral site substituting Cr. It is worthwhile to note that chromites are in co-existence with olivine and pyroxene; minerals deficient in Al. It is also noted that

plagioclase is almost negligible in the ultramafics which host chromite. Since Al scavenging minerals did not precede chromite crystallization, the Al remained in the residual magma and along with Fe^{3+} substituted Cr during the late stage of chromite crystallization.

Individual grains from the different ore bodies were also analysed by EPMA to exhibit compositional variation between the two stages of chromite crystallization (Table 2).

Table 2. EPMA data of chromites from different lodes.

Oxides	Durga	Laxmi	Shankar	Ganga
Cr_2O_3	62.47	62.342	62.232	25.963
FeO	11.30	11.475	11.842	57.212
MgO	16.77	16.623	15.805	0.613
Al_2O_3	8.14	8.467	8.608	8.822
TiO_2	0.134	0.142	0.146	0.824
V_2O_5	0.003	0.003	0.003	0.007
NiO	0.105	0.100	0.099	0.255
Total	98.923	99.152	98.735	93.696

From the Table 2, it is observed that late stage chromite from Ganga ore body is rich iron and titanium compared to the early stage chromite from other three ore bodies.

Due to a combined effect of temperature, oxygen fugacity and relative concentration of cations during the whole course of chromite crystallization, the early and late stage chromites show significant differences in chemical composition reflecting their trivalent and divalent cations content at both octahedral and tetrahedral sites respectively (Table 3).

Beneficiation Characters

Besides exhibiting physical and chemical differences, the chromites belonging to early and late stages also show variations in their beneficiation characteristics. The early stage chromites are easy to beneficiate because they are associated with serpentine; altered product of olivine. Serpentine is a hydrous magnesium silicate and possesses contrasting physical properties. It is nonmagnetic and has lower specific gravity contrary to the high specific gravity of chromite. These chromites are easy for beneficiation by gravity and heavy media separation methods. By this process a good concentrate with high Cr:Fe ratio and Cr_2O_3 can be obtained. The mineralogical study indicates that the late stage chromites are mostly associated with talc, tremolite and chlorite. The silicate gangues are fibrous and very fine grained. It is very difficult to separate the fine gangue from the chromite. Besides chlorite, which is associated with chromite; exhibits magnetic behaviour similar to the associated chromite. So beneficiating the late stage chromites by gravity, heavy media and magnetic methods are not fully successful. In order to get a pure concentrate, a combination of methods such as heavy media, gravity, magnetic and acid treatment is required. So from the laboratory beneficiation tests, it is observed that early stage chromites are easy to beneficiate compared to the late stage chromites.

CONCLUSIONS

In Boula - Nausahi igneous complex, chromite layers are confined to ultramafic rocks (now altered to

Table 3. Cation distribution in chromites from Boula-Nausahi Igneous complex

Sl.No.	Cr	Al	Fe ³⁺	Ti	V	Mg	Fe ²⁺
1	12.44	1.64	1.824	0.08	0.016	4.96	3.04
2	12.1	2.39	1.37	0.112	0.032	4.35	3.65
3	11.408	2.808	1.768	0.048	0.016	4.608	3.392
4	11.36	2.832	1.656	0.048	0.016	4.664	3.336
5	11.272	3.008	1.656	0.048	0.016	4.496	3.504
6	11.392	2.936	1.56	0.072	0.04	4.096	3.904
7	11.136	3.168	1.64	0.08	0.048	3.816	4.184
8	10.96	3.36	1.536	0.096	0.048	3.64	4.36
9	11.024	3.096	1.856	0.064	0.032	4.16	3.84
10	11.032	3.2	1.672	0.064	0.032	3.936	4.064
11	11.016	3.08	1.792	0.064	0.04	4.024	3.976
12	10.912	3.064	1.912	0.064	0.048	3.72	4.28
13	10.856	3.744	1.24	0.112	0.048	3.568	4.432
14	10.864	3.52	1.456	0.112	0.048	3.776	4.224
15	10.872	2.752	2.232	0.096	0.048	3.848	4.152
16	10.832	2.896	2.096	0.128	0.048	4.08	3.92
17	10.768	3.008	2.12	0.064	0.048	4.2	3.8
18	10.712	3.544	1.664	0.048	0.032	4.048	3.952
19	10.68	3.136	2.048	0.08	0.048	4.24	3.76
20	10.296	3.136	2.4	0.112	0.048	4.208	3.792
21	10.28	4.264	1.256	0.144	0.064	3.376	4.624
22	10.224	4.44	1.168	0.12	0.048	3.464	4.536
23	9.936	4.032	1.924	0.144	0.064	2.708	5.296
24	9.272	3.192	3.464	0.08	0.032	3.6	4.4
25	8.42	3.46	3.95	0.144	0.016	3.42	4.58
26	7.6	2.056	5.92	0.352	0.064	3.136	4.864
27	6.12	3.64	6.36	0.528	0.064	2.392	5.608
28	5.344	3.552	6.496	0.512	0.096	2.296	5.704
29	4.928	3.424	7.012	0.528	0.096	2.144	5.586
30	4.55	3.66	6.94	0.544	0.08	2.03	5.97

serpentinite, talc, tremolite, chlorite assemblage). The grain size distribution indicates a continuous crystallization process. However the chemical characters reveal two stages of chromite crystallization. Besides the chemical differences, the chromites representing two stages also exhibit differences in their average grain size, reflectivity, associated silicate mineralogy, their composition, cell dimension, magnetic behaviour and beneficiation characteristics. The early chromites are generally coarse grained and associated with olivine. Their cell dimensions vary from 8.27 to 8.29 Å and they are nonmagnetic. On the contrary, the late stage chromites are fine grained, associated with pyroxene. They are magnetic and have cell dimension around 8.39 Å. The chemical data

indicate that early stage chromites have formed at a higher temperature and low oxygen fugacity conditions than the late stage chromites. Lower temperature and oxidising conditions prevailing during the late stage crystallization facilitated significant cationic substitution both at tetrahedral and octahedral sites in the late stage chromites. The early stage chromites are easy to beneficiate compared to the late stage ones which require complex beneficiation operations.

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