FURTHER DATA ON THE CHEMICAL COMPOSITION OF ZHOB VALLEY CHROMITES[1]

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ABSTRACT

The general geology, including broad structural features, of the Zhob Valley igneous complex is described. The observed field relationships of the rock types and characteristics exhibited by chromite deposits point to the complex being of an Alpine type. Seven new chemical analyses together with trace elements are given, and the possible mode of formation of these chromite deposits is discussed.

INTRODUCTION

The Zhob Valley igneous complex in West Pakistan is exposed over an area of more than 2000 square miles, although the complete extent is not yet known. The westernmost outcrops of the igneous complex are near Khanozai in Quetta-Pishin district (Fig. 1), and the best exposures are to be seen in Hindubagh-Nasai area in the Zhob district, where some of the larger hills, such as Jungtorghar and Saplaitorghar, consist almost entirely of these rocks. From Killa Saifullah to Fort Sandeman local outcrops occur along the road, and from 12 miles north of Fort Sandeman to the Afghanistan border there is scattered development of these rocks.

PREVIOUS WORK

Little is known of the geology of the complex or the chemical composition of the chromites from this area. A preliminary description of mineralogy and petrology of the central part of the complex near Hindubagh has been given earlier (Bilgrami, 1962), and preliminary chemical data on the Zhob Valley chromites have been given by Bilgrami and Ingamells (1961). Recently Bogue (1962) has given seven chemical analyses from this complex, and seven new chemical analyses together with trace elements are presented here.

GEOLOGY AND OCCURRENCE

The Zhob Valley igneous complex consists of serpentinites, dunites, harzburgites, and other varieties of peridotite, pyroxenites, anorthosites, troctolites and gabbros, all cut by later dikes of dolerite, rodingite and albitite. In Fort Sandeman area rhyolite dikes are also found. The igneous complex is intrusive into sediments (limestones, shales and sandstones) of Triassic to Eocene age. At the contacts with the sediments, metamorphic rocks such as marbles, hornblende schists and gneisses and

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hornblende-epidote-albite schists are developed. The general trend of the igneous rocks is ENE-WSW. The age of the complex has not been determined definitely and it is possible that the rocks in various localities may differ in their ages. It is further suggested that some of the serpentinites of the area were emplaced tectonically, thereby further complicating the age relationships.

Chromite mining was started in 1902 and has continued since, with a break during 1931–1933. The average yearly production has been between 20,000 and 30,000 tons. Workable chromite deposits fall in two categories:

(i) Stringers, bands and lenses composed almost wholly of chromite with minor amounts of serpentine.

(ii) Serpentinized dunite exceptionally rich in chromite. These may be either serpentines with disseminated chromite grains or thin bands of chromite separated by barren or almost barren rock (Fig. 2).

In bands, the chromite occurs as closely packed grains with a little interstitial serpentine (Figs. 3, 4). These are mostly low-grade ores. Most
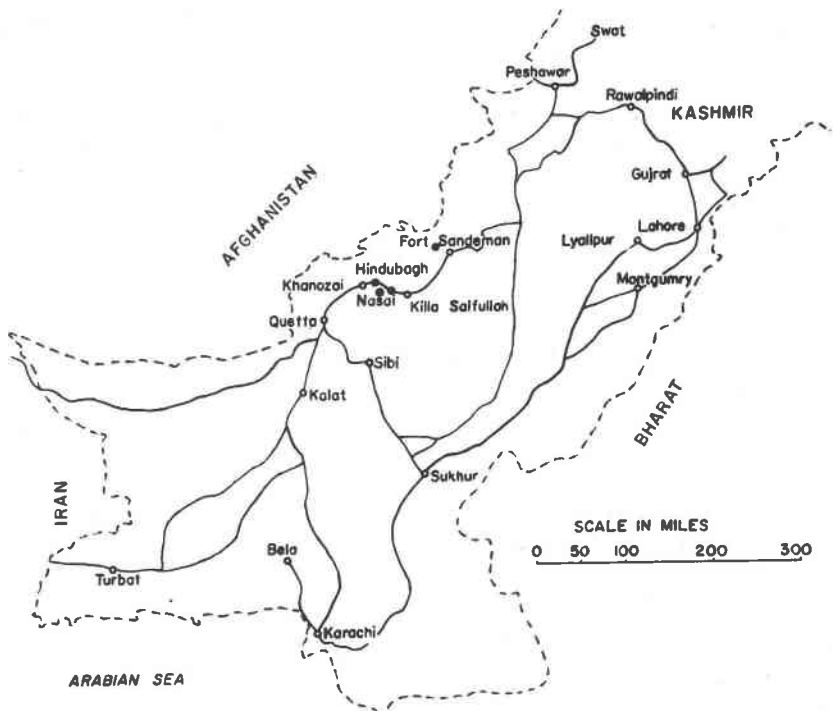

Fig. 1. Map of West Pakistan showing location (solid circles) of the specimens described in this paper.
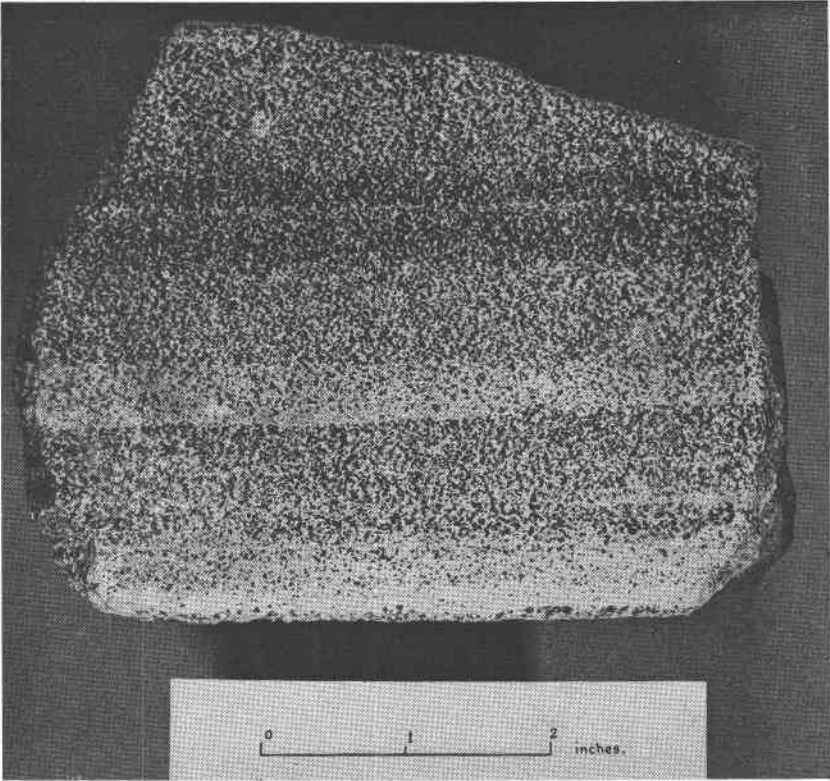
Fig. 2. Serpentine with disseminated grains of chromite
showing imperfect banding. (Mine 40 DMC.)

of the chromite layers and bands are sharply separated from serpentine or harzburgite, with which they are associated, commonly with slickensided surfaces.

The bands, layers and lenses of chromite do not show any apparent directional relationship with the boundaries of the intrusive and seem to be distributed at random in the host rock. In places, however, there seems to be a definite relationship between the layering in the ultramafics and the chromite layers. On the west side of Jungtorghar the chromite layers are parallel to the dunite-harzburgite layers and dip in the same direction as the ultramafic rocks. The bands and lenses of chromite are spread over large areas and vary in length and breadth from a fraction of a centimeter to several meters. The serpentine between the bands of chromite is pale yellowish-green in color and may or may not be free of chromite. A different type of banding is one described as "grape shot ore" (Fig. 5), in

which globules of chromite are enclosed in a pale-green serpentine. The globules vary in diameter from a fraction of a centimeter to two or three centimeters; larger globules have been found in the past. It is noteworthy that individual globules are not deformed, and this strongly suggests that the grape shot ore exhibits a primary texture. The proportion of globules to serpentine varies considerably; 5 to 95 per cent of globules in bands has been observed. In a few cases grape shot ore grades into bands of massive chromite which seem to have been produced by squashing of the globules. The reverse relationship, that of serpentine globules in chains of chromite, has also been noted (Fig. 6). Some of the specimens show a slightly modified settled texture, whereas in others an ill-defined gneissic banding is developed due to deformation of olivine (now serpentine) blobs or globules.
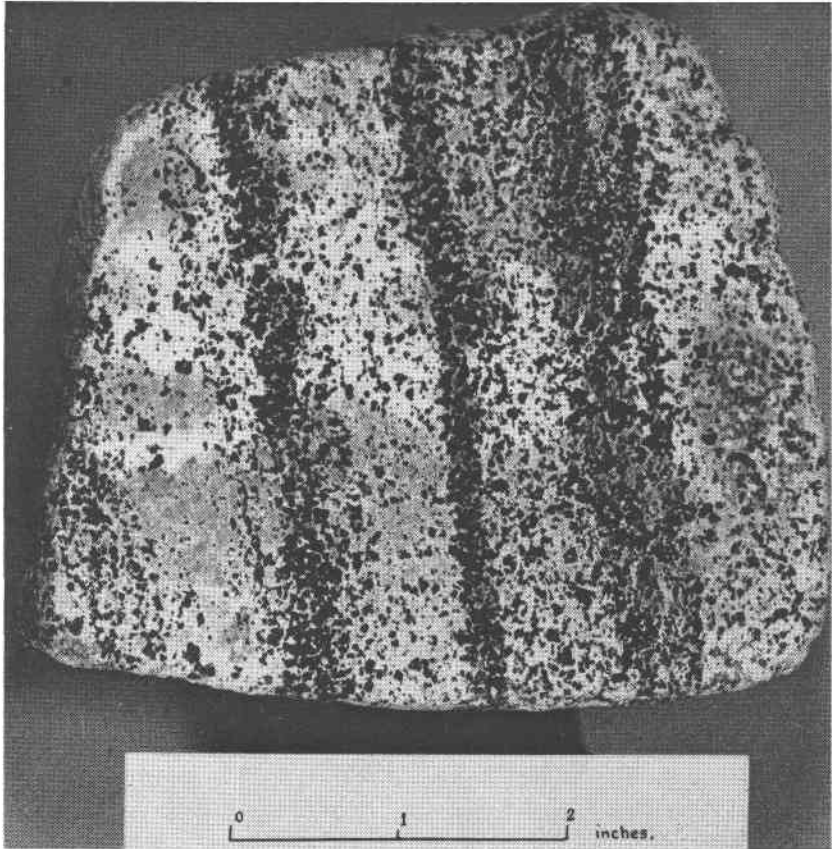

FIG. 3. Specimen showing chromite-rich bands separated by serpentine with disseminated chromite grains. (Mine 88.)
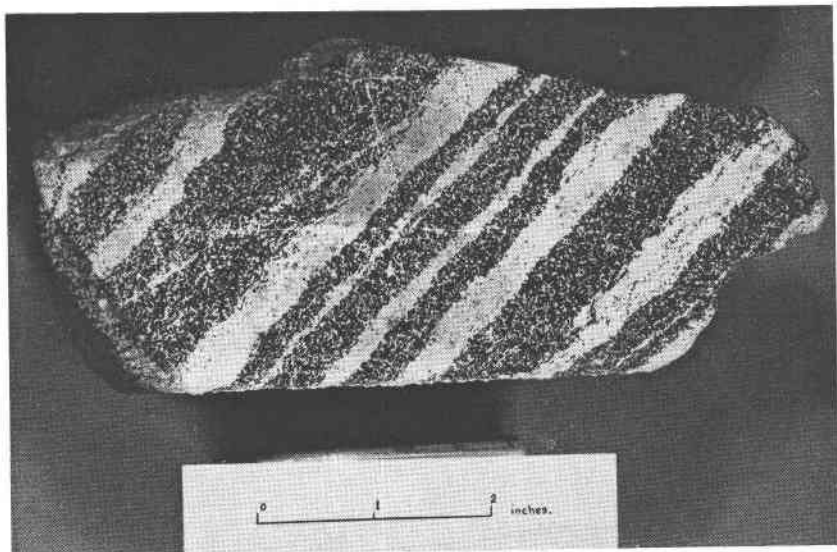
Fɪɢ. 4. Specimen showing bands of chromite separated by pale yellowish green serpentine with few disseminated grains of chromite. (Mine 7ML/1.)

Thayer (1960) has recently given characteristic features for distinguishing stratiform peridotite-gabbro complexes from those of the Alpine type. Since the detailed geology of the Zhob Valley igneous complex has not been worked out, it is not possible here to give all of its characteristics. Many of the features exhibited by the rocks of this complex point to its being of the Alpine type. The irregular distribution of various rock units, the generally lenticular character of the chromite layers and bands, the abundance of peridotite with dominant olivine, the scarcity of plagioclase in the ultrabasic rock units, the high $MgO:FeO$ ratio in the rocks (Bilgrami, 1962), and the high $Cr:Fe$ ratio in the chromites (Table 2) all point to the complex being of the Alpine type. The abundance of genetically related dikes (Bilgrami, 1962) is yet another evidence in favor of its being classed as an Alpine type of complex. The ultramafic rocks show ample evidence of crushing in the hand specimen as well as in thin section. A complete absence of zoning in the peridotite and harzburgite minerals is remarkable in view of the fact that plagioclase and pyroxene in the dolerites exhibit this structure abundantly. Gneissic structure in chromite is quite common (Fig. 7) and further points to these chromite deposits being of the Alpine type. One feature not characteristic of Alpine type complexes is however present: the contact metamorphic effects are quite marked at many places, and even assimilation of shales by the ultramafic rocks has taken place (Bilgrami, 1962).

Layering is shown in a few localities but is very limited in extent. Rhythmic and cryptic layering are also exhibited by chromite bands and veins, but this too is very localized. The layers are only a few centimeters thick and are seldom more than a few meters long. In discussing the origin of layering in the rocks of the Stillwater Complex (Hess, 1956, p. 449) has pointed out that convection currents must have existed. Jackson (1961, p. 83) however, holds that "All the varieties of layering in the ultramafic zone of the Complex are fundamentally related to the action of gravity on dispersed crystals of the three primary precipitate minerals." In the case
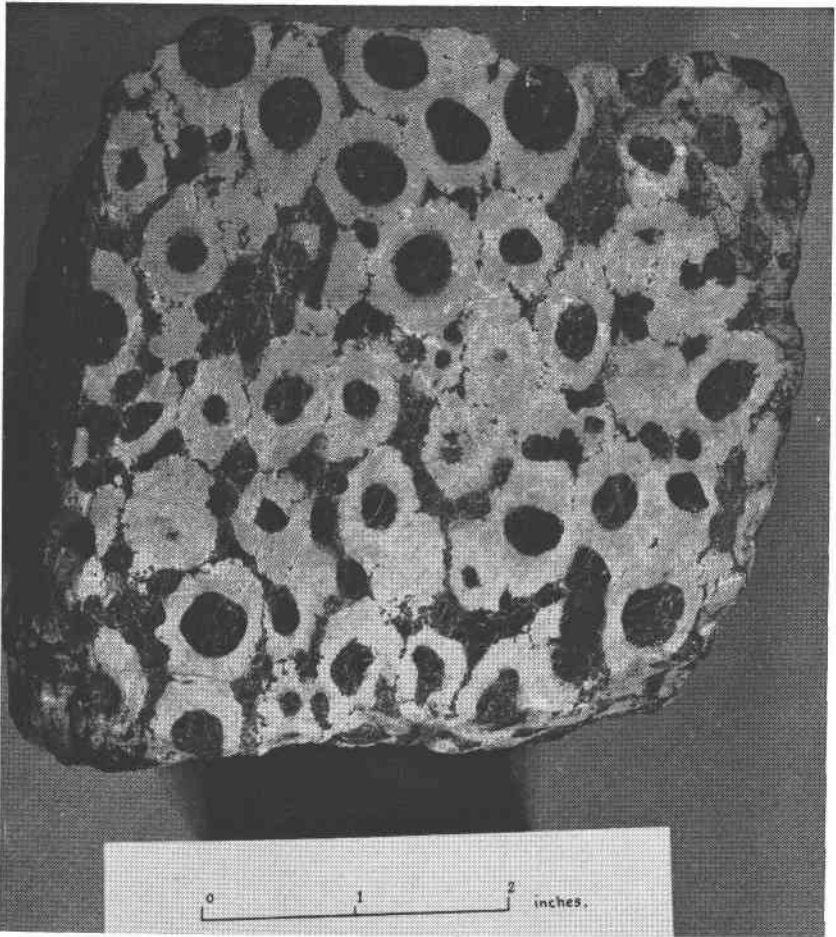

FIG. 5. Grape shot ore showing orbicular texture (mine No. 166). Note that "chains" of chromite are developing by squashing of chromite globules. This is a primary undeformed texture.
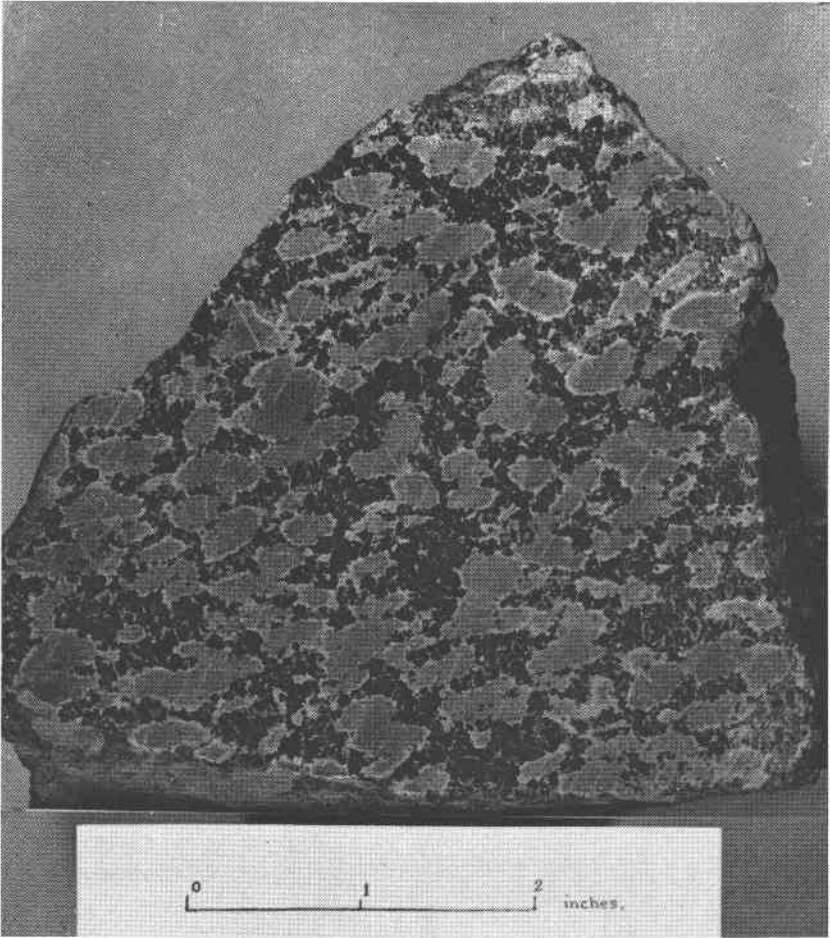
FIG. 6. "Eyes" of serpentine in chains of chromite. This appears to be a slightly modified settled texture of chromite interstitial to large olivines, the whole somewhat sheared along a plane sloping 20°–30° to the left in the photograph.

of the Zhob Valley complex no evidence for convection currents has been found, and it is assumed that gravitative settling of crystallizing minerals played an important part in the production of banded structures exhibited by these ultramafic rocks.

In thin section two types of chromites have been recognized:

(i) Showing euhedral and anhedral forms, dark brown (translucent) color and traversed by numerous irregular veins of colorless serpentine. The chromite grains usually contain inclusions of colorless serpentine or chlorite, some pseudomorphous after olivine.

(ii) The other type of chromite is a completely opaque variety which also shows euhedral and anhedral forms and is traversed by veins of serpentine, possibly replacing original olivine.

It has been suggested by Kramm (1910), Dresser (1913) and Phillips (1927) that the opaque variety has been formed by the alteration of picotite. No evidence of this has been found in the Zhob Valley chromites. However a golden-brown spinel traversed by veins of an opaque variety is found in most harzburgites. The dark variety of spinel may either be chromite or magnetite. Dresser (1913) has also suggested that the opaque chromite is highly ferruginous, whereas the translucent variety is rich in magnesium, a suggestion confirmed by the chemical analyses of the Zhob Valley chromites (Table 1).

Chemical Analyses of the Zhob Valley Chromites

Seven new chemical analyses of the Zhob Valley chromites are given in Table 1. The analyses were carried out on cleaned chromites by the
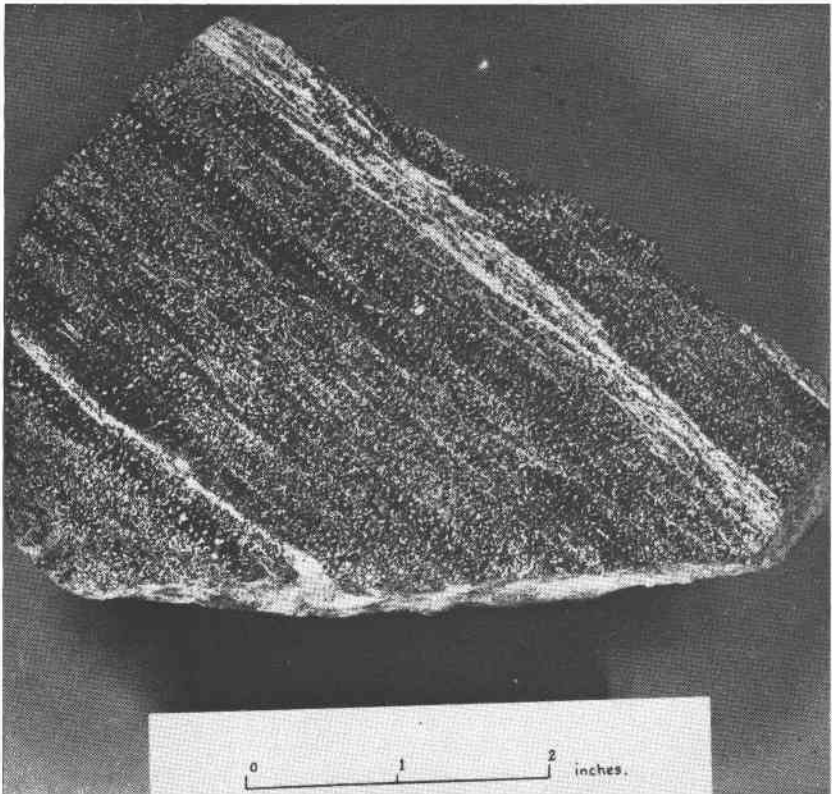

Fig. 7. Low grade chromite showing gneissic banding. (Mine 34ML.)

TABLE 1. CHEMICAL ANALYSES OF ZHOB VALLEY CHROMITES
(Analyst S. A. Bilgrami)

	1	2	3	4	5	6	7
Cr_2O_3	58.72	54.41	53.91	56.21	55.79	54.45	45.21
Al_2O_3	11.64	13.86	13.35	12.69	11.05	11.32	20.24
Fe_2O_3	5.36	3.98	3.46	3.16	4.68	4.84	4.41
TiO_2	0.16	0.45	0.26	0.24	0.19	0.21	0.21
V_2O_5	0.06	0.07	0.08	0.08	0.04	0.14	0.12
FeO	8.47	12.26	13.89	13.84	13.94	14.65	14.26
NiO	0.23	0.16	0.09	0.17	0.14	0.12	0.21
MgO	14.52	14.24	13.86	12.57	13.56	13.24	15.12
MnO	0.17	0.20	0.18	0.19	0.20	0.19	0.25
CaO	Trace	0.08	0.07	0.08	Trace	0.02	0.01
H_2O+	0.25	0.21	0.19	0.18	0.12	0.14	0.06
SiO_2	0.21	0.24	0.29	0.26	0.22	0.25	0.31
	99.79	100.16	99.61	99.67	99.93	99.57	100.41

Specimens from mines:

1. 135 —Medium-grained, disseminated chromite grains in a matrix of pale yellow serpentine. Coffee-brown translucent in thin section.

2. 136 —Coarse-grained, massive ore in serpentized dunite. Coffee-brown in thin section.

3. 208 —Jet black massive ore, sheared and brecciated.

4. 7ML/1 —Coarse-grained, massive ore, locally banded and associated with serpentized dunite.

5. 40DMC⎫
6. 221 ⎭ —Disseminated medium grained ore, locally banded, associated with yellow or dark-gray serpentine.

7. East of Jallat —Hard, compact, coarse-grained ore showing metallic luster and
Killi, Fort associated with green serpentine.
Sandeman

Nos. 3 to 7 jet black and opaque in thin sections.

techniques previously described by Bilgrami and Ingamells (1961). Chromites from various localities show some characteristic features; thus Jungtorghar chromite (Table 1, anal. I) is characterized by high Cr_2O_3, MgO, Fe_2O_3 and low Al_2O_3 and FeO. The Saplatorghar chromites (anals. 2, 3, 4) show moderately high Cr_2O_3, Fe_2O_3, and FeO but a lower MgO content than Jungtorghar chromites. The Nasai chromites (anals. 5, 6) show high Cr_2O_3 and total iron content. However the total iron is fairly uniform in all the chromites from these three localities. Analysis 7 is of a

chromite from Fort Sandeman area, about 144 miles ENE of Hindubagh. This chromite has a lower Cr_2O_3 content and high Al_2O_3 and total iron. Chromites with comparable Al_2O_3 content have not been found elsewhere in the Zhob Valley.

The structural formulae of the Zhob Valley chromites calculated on the basis of 16(0) are given in Table 2. In calculating the structural formulae the procedure recommended by Stevens (1944) was followed, although correction was made for ilmenite by taking out from the molecular proportions FeO equivalent to TiO_2. It will be seen from the structural formulae given in Table 2 that the summation of the trivalent group is lower than the ideal value of 8 in all but two chromites. This variation may be due entirely to analytical error or may suggest that not all chromites of the Zhob Valley complex crystallized under similar conditions.

Thayer (1946) has discussed in detail the various factors that might influence the chemical composition of chromites. The Zhob Valley chromites are mostly found in dunite and hence are rich in Cr_2O_3 and MgO and poor in Al_2O_3. There is, however, a definite trend of compositional vari-

TABLE 2. STRUCTURAL FORMULAE OF THE ZHOB VALLEY CHROMITES.
CATIONS ON THE BASIS OF 16 (0)

|	1	2	3	4	5	6	7
Cr	5.925	5.498	5.504	5.767	5.726	5.623	4.415
Al	1.751	2.088	2.032	1.941	1.696	1.721	2.953
Fe^{3+}	0.518	0.383	0.336	0.308	0.456	0.476	0.411
V	0.005	0.006	0.007	0.006	0.003	0.012	0.010
Fe^{2+}	0.890	1.233	1.471	1.479	1.494	1.580	1.453
Mg	2.760	2.712	2.666	2.432	2.621	2.573	2.787
Ni	0.024	0.016	0.009	0.018	0.014	0.012	0.020
Mn	0.018	0.060	0.019	0.021	—	0.060	0.026
Ca	—	0.012	0.018	0.012	—	0.003	0.001
(Cr, Al, Fe^{3+}, V)	8.199	7.975	7.879	8.022	7.882	7.832	7.789
$(Fe^{2+}$, Mg, Ni, Ca)	3.860	4.024	4.183	3.915	4.150	3.962	4.228
RO/R_2O_3	0.907	1.002	1.061	0.988	1.054	1.068	0.923
Cr/Fe	3.90	3.03	2.74	2.99	2.71	2.38	2.47
MgO/RO	2.92	1.94	1.75	1.64	1.71	1.66	1.84

Nos. same as in Table 1.
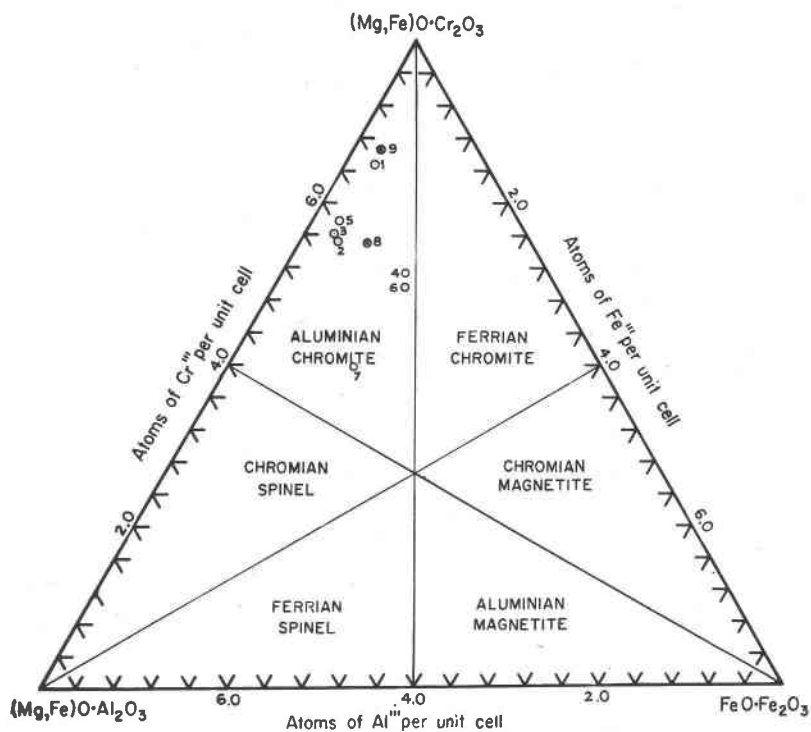
FIG. 8. Triangular diagram showing variation in the chemical composition of Zhob Valley chromites.

ation as we proceed from west to east; Cr_2O_3 and MgO decrease and total iron increases generally eastward. This also explains the variation in the Cr/Fe ratio of the Zhob Valley chromites. The chromite from Fort Sandeman is very rich in Al_2O_3, and this may be due to a general high Al_2O_3 content of the host rocks. Gabbros and even acid rock types are known to occur in the Fort Sandeman area, and increased availability of Al_2O_3 in the magma may be responsible for high Al_2O_3 content of this chromite.

The wide range in the chemical composition of chromite, due to variation in ratios of FeO to MgO and Cr_2O_3 to Al_2O_3 and Fe_2O_3 can be adequately shown on a triangular diagram devised by W. D. Johnston, Jr. and described by R. E. Stevens (1944). Figure 8 is a plot of nine chromite analyses from the Zhob Valley igneous complex. It will be seen that the chromites show a considerable range in composition. Generally speaking, chromites from Jungtorghar (Nos. 1 and 9) fall closest to the theoretical chromite molecule. Saplaitorghar and Nasai chromites (Nos.

2, 3, 8, Fig. 8) fall almost in the middle of chromite field. Specimens 4 and
6 fall very close to the field of ferrian chromite. Fort Sandeman chromite
(No. 7) is close to chromian spinel field. It is noteworthy that all chro-
mites described here fall on chromite-spinel tie line.

Expression of analyses in terms of end members. The chemical analyses of
the Zhob Valley chromites expressed in the form of end-member formula
and weight percentages are given in Table 3. The end-member formula
percentages have been obtained by the formula given by Stevens (1944).
The weight percentages have been obtained by multiplying the unit cells
by their molecular weights and recalculating to 100 per cent. It will be
seen from Table 3 that the Zhob Valley chromites exhibit a considerable
range in composition. Spinel varies from 14.9 to 33.5 per cent. Variations
in magnesio- and ferrochromites are very considerable, but the maximum
variation is shown by magnetite, which varies from 4.2 to 17.7 per cent.

Thayer (1961) has pointed out that normative chromite varies from
20–80% and spinel from 15–80% in chromites from Alpine type com-
plexes. Chromite 1 (Table 3) has 80.7 per cent normative chromite and is
thus close to the boundary limit given by Thayer. Another specimen from
the same locality described earlier (Bilgrami and Ingamells, 1961, Table
1, anal. 1) is even higher (83.7 per cent) in normative chromite (Fig. 8,
No. 9).

Distribution of trace elements. In all, eighteen elements were looked for; of
these the eight that are present were quantitatively determined spectro-
chemically by the methods already described (Bilgrami, 1961). Table 4
shows the results of spectrochemical analyses: Co, Ni, V, Cu, Zr, Ga, Ba,

TABLE 3. END MEMBER FORMULA PERCENTAGES OF ZHOB VALLEY CHROMITES

	1	2	3	4	5	6	7
Spinel	14.95	26.21	25.80	24.20	19.02	19.27	33.47
Magnesiochromite	32.23	41.65	41.82	36.48	39.77	38.39	29.73
Ferrochromite	48.49	27.14	28.20	35.48	24.45	24.63	20.34
Magnetite	4.32	4.86	4.24	3.84	16.76	17.71	16.46
End Member Weight Percentages							
Spinel	15.06	26.94	26.48	19.53	19.32	19.53	33.72
Magnesiochromite	29.16	38.42	38.55	34.95	36.29	34.95	26.91
Ferrochromite	51.07	29.24	30.26	26.10	25.97	26.10	21.43
Magnetite	4.71	5.40	4.71	19.42	18.42	19.42	17.94

Nos. same as in Table 1.

TABLE 4. DISTRIBUTION OF TRACE ELEMENTS IN ZHOB VALLEY CHROMITES
(WEIGHT PERCENTAGES)
(Analyst S. A. Bilgrami)

Specimen No.	CoO	NiO		CuO
1	0.015	0.16	0.07	0.0015
2	0.014	0.23	0.06	0.0014
3	0.015	0.09	0.08	0.0009
4	0.013	0.14	0.04	0.0017
5	0.012	0.17	0.08	0.0020
6	0.009	0.12	0.14	0.0016
7	0.011	0.21	0.12	0.0021

In all specimens: Zr 0.0015%, Ga 0.00015%, Ba 0.0003%, Sr 0.0003%. Looked for but not detected: Ag, Au, Be, Ge, Mo, Pd., Pt, Sn, U, Os.

Nos. same as in Table 1.

and Sr, are present; Ag, Au, Be, Ge, Mo, Pd, Pt, Sn, U, and Os are either absent or present below the sensitivity limit of the method adopted.

Cobalt shows considerable variation and ranges from .009 to .015 per cent. There does not seem to be any correlation between this and any major element in the chromites.

Nickel varies from .09 to 0.23 per cent and appears to follow Mg generally. It is suggested that Ni exists in chromite molecule replacing Mg or Fe^{2+}.

Vanadium also shows considerable variation and appears to be related to Fe_2O_3 content of chromites. This may be present as replacing Fe^{3+} or Cr.

Copper occurs in very minute amounts and does not appear to be related to any major element.

GENERAL DISCUSSION

In an earlier paper (Bilgrami, 1962), it has been stated that the field observations generally support the Bowen and Tuttle (1949) theory that these rocks were intruded as a crystal mush. Thayer (1960) has pointed out that there is overwhelming evidence against the formation of Alpine ultramafic bodies by fractional crystallization of a gabbroic magma *in situ*. Since detailed geology of the Zhob Valley Complex is not known, it is not possible here to examine critically the various criteria given by Thayer (1960, p. 182) as being evidence against the formation of ultramafic bodies by fractionation of a gabbroic magma *in situ*.

Various investigators have reported the existence of ultramafic magmas. Duparc (1920) has described the ultramafic complexes of the Ural mountains, and from his description it seems reasonable to conclude that these rocks were formed by the intrusions of gabbroic and ultra-

mafic magmas. Hess (1938, 1948) has described parallel belts of serpentine intrusions which are concentrically zoned and are free of chromite. Walton (1951) has proposed the intrusion of peridotitic magma in the Blashke Islands Complex. The variations in the rock types of the Union Bay Complex have been explained by Ruckmick and Noble (1959) as due to intrusion of successive gabbroic, pyroxenitic and dunitic magmas. Irvine (1959) has suggested that in the Duke Island ultramafic complex intrusion of gabbroic and olivine pyroxenitic magmas took place. Wager and Deer (1939), Cameron and Emerson (1960), Jackson (1961) and many others have described ultramafic complexes which have been formed by crystallization differentiation from a fluid magma of basic composition. Thus we have conclusive evidence of two different modes of formation of ultramafic complexes. There appears to be insufficient appreciation of the fact that all the ultramafic complexes have not been formed by similar processes or from similar magmas. There are thus peridotites and peridotites. In the Zhob Valley igneous complex a great variety of rocks exists, and, whereas the relationships between the rock types have not been worked out, it seems that these rocks were intruded as an already differentiated crystal mush. The observed metamorphic effects could be explained as being due to the heat of the interstitial liquid which also, in places, assimilated shale at the contact. As has been suggested elsewhere (Bilgrami and Ingamells, 1961) the chromites rich in Cr_2O_3 and MgO and showing a Cr:Fe ratio of better than 3:1 are regarded as earlier in age than those with a lower ratio. Work on this complex is continuing, and it is hoped that more data will be presented in the near future.

Acknowledgments

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