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CHEMICAL COMPOSITION OF THE ZHOB VALLEY CHROMITES, WEST PAKISTAN

S. A. BILGRAMI AND C. O. INGAMELLS,* *Department of Geology, University of Minnesota, Minneapolis.*

ABSTRACT

Two complete and 22 partial chemical analyses of chromites from the Hindubagh-Nasai area in West Pakistan are given, and their chemical composition is discussed. It is suggested that the chromites showing a Cr/Fe ratio greater than 3:1 are earlier in age than those showing a lower ratio. A new method for the complete chemical analysis of chromite is described.

INTRODUCTION

The Zhob Valley igneous complex in West Pakistan occupies an area of over 2000 square miles, although the actual extent is not known. The first outcrops of the igneous complex are near Khanozai in Quetta-Pishin district (Fig. 1) and the best exposures are seen in Hindubagh-Nasai area in the Zhob district, where some of the larger hills like Jungtorgarh and Saplaitorgarh consist almost entirely of these rocks. From Killa Saifullah to Fort Sandeman occasional outcrops occur along the road, and from 12 miles north of Fort Sandeman to the Afghanistan border there is an almost continuous development of these rocks.

Little is known of the geology of the complex or the chemical composition of the chromites from this area. A preliminary description of the mineralogy and petrology of the Hindubagh area has been given (Bilgrami, 1960), and the present paper is the first attempt at discussing the chemical composition of the Zhob Valley chromites. About 30,000 tons of high-grade chromite are produced annually in the Zhob Valley, of which over 99 per cent comes from Hindubagh-Nasai area. All the samples described here have been collected from this area.

GEOLOGY AND OCCURRENCE

In the Hindubagh-Nasai area the igneous complex consists of serpentinites, dunites, harzburgites, peridotites and chromitites, all cut by later diabase dikes. The igneous complex is intrusive into sediments (limestones and shales) of Triassic to Eocene age. At the contacts with the sediments, metamorphic rocks such as crystalline limestones, hornblende schists and gneisses, and albite-epidote-hornblende schists are developed. The general trend of the igneous rocks is ENE-WSW. These rocks are believed to be of Eocene age in the Hindubagh area.

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* Present address, College of Mineral Industries, Penn. State University, University Park, Penn.

Economically workable chromite deposits fall in two catagories:

(a) Veins, bands and lenses composed wholly of chromite with minor amounts of serpentine.

(b) Serpentinized dunite occasionally rich in chromites. These are mostly low-grade ores. Both types are sharply separated from serpentine or harzburgite, with which they are associated, often with slickensided surfaces.

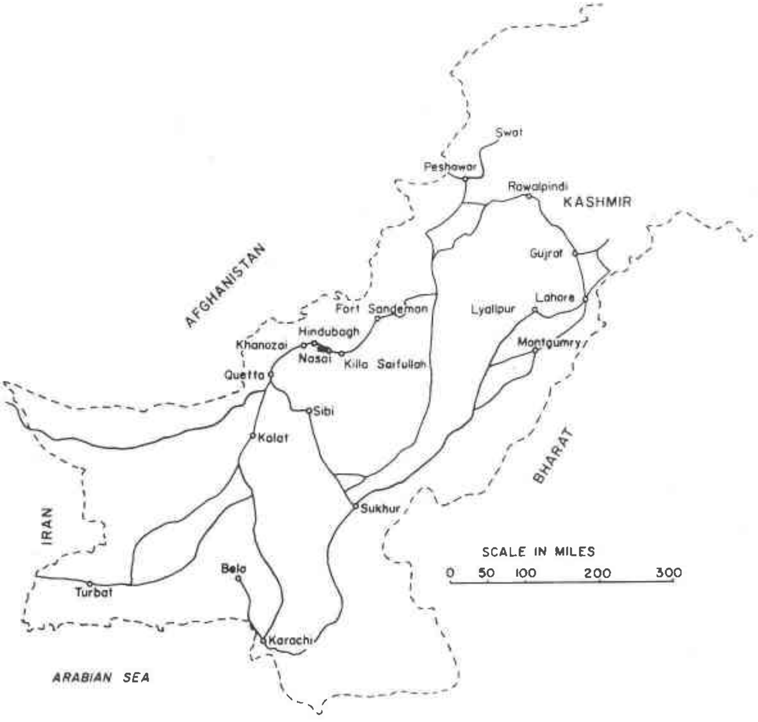

FIG. 1. Map of West Pakistan, showing the location of Hindubagh-Nasai area (black rectangle).

The bands, veins and lenses of chromite which do not show any directional relationship with the boundaries of the intrusives often show parallelism among themselves. The bands, veins and lenses are spread over wide areas and vary in length and thickness from a fraction of a centimeter to several meters. The serpentine in between the bands of chromite is pale yellowish-green in color and may or may not be free from chromite. A different type of banding is one described as "grape-shot ore" where globules of chromite are enclosed in pale-green serpentine. These globules vary in diameter from a fraction of a millimeter to two or three meters. Larger globules have been found in the area in the past.

In thin section two types of chromites have been recognized:

(a) Showing anhedral form, dark brown (translucent) color and traversed by numerous irregular veins of serpentine. The crystals usually contain inclusions of colorless serpentine or chlorite, some pseudomorphous after olivine.

(b) The other type of chromite is a completely opaque variety which also shows anhedral form and is traversed by serpentine veins, 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. Dresser (1913) has also suggested that the opaque chromite is highly ferruginous, while the translucent variety is rich in magnesium, a suggestion confirmed by the chemical analyses of the Zhob Valley chromites (Tables 1, 4 and 6).

Chemical Analyses of the Zhob Valley Chromites

Chemical analyses of two chromites from Hindubagh area are given in Table 1. Unfortunately after the analyses had been started it was discovered that the samples were not pure, and because only small quantities had been brought from Pakistan, further samples were not available for purification. The low totals of the two analyses may be due to presence of elements which could not be determined due to the nonavailability of the sample. Nickel is present in both but could not be determined. Zinc has been reported in chromites (Donath, 1931, 484) but was not estimated in the samples from Hindubagh.

Both the samples under consideration show high Cr_2O_3 and MgO contents. The first sample (B-327) is low in total iron and high in Al_2O_3 compared to the second sample (B-353). In fact the low Al_2O_3 content of the second sample (B-353) is a rare feature and a review of the published analyses has shown that chromites with comparable Cr_2O_3 content have a higher Al_2O_3 content (Table 1, anal. 5).

The structural formulae of the Hindubagh chromites calculated on the basis of 32(O) are given in Table 2. In calculating the structural formula of sample B-327 the procedure recommended by Stevens (1944) was followed, while in the case of B-353 corrections were made for serpentine and ilmenite by taking out from the molecular proportions MgO twice the amount of SiO_2 for serpentine, and FeO equivalent to TiO_2 for ilmenite. The molecular proportions were then recalculated to an arbitrary total of 0.5, and from the recalculated molecular proportions the struc-

TABLE 1. CHEMICAL ANALYSES OF THE ZHOB VALLEY CHROMITES WITH COMPARISONS

	1	2	3	4	5
Cr_2O_3	57.43	52.17	56.46	57.83	52.18
Al_2O_3	9.37	5.28	12.35	9.90	10.80
Fe_2O_3	6.16	2.56	3.35	4.05	4.53
TiO_2	0.23	0.20	0.23	0.06	0.26
FeO	9.99	15.30	11.05	14.98	20.67
MnO	0.38	0.98	trace	0.20	0.32
MgO	14.17	13.43	15.38	12.55	9.58
CaO	0.04	0.06	trace	0.06	0.10
V_2O_5	0.04	0.11	—	—	—
NiO	p.n.d.	p.n.d.	—	—	—
SiO_2	0.80	5.44	1.34	0.16	0.88
H_2O+	0.86	2.63	—	0.36	0.40
	99.42	98.16	100.16	100.09	99.72
Cr	39.29	35.69	38.66	39.59	37.08
Fe	12.09	13.78	10.93	14.48	19.22
Cr/Fe	3.24	2.88	3.54	2.73	1.93
RO/R_2O_3	0.99	1.36	1.00	1.02	1.05
Impurity;	Serpentine	Serpentine	Talc	Olivine	Olivine

1. Chromite (B-327), Mine 132, Jungtorgarh, Hindubagh. Analyst, C. O. Ingamells.
2. Chromite (B-353), Mine 136, Saplaitorgarh, Hindubagh. Analyst, C. O. Ingamells.
3. Chrome ore produced by Baluchistan Chrome Co., Hindubagh (Malhotra and Prasada Rao, 1956, 465, anal. 2). Analyst, P. D. Malhotra.
4. Chromite from high-grade ore deposit, Red Mountain, Kenai Peninsula, Alaska. (Stevens, 1944, 6, anal. 3). Analyst, R. E. Stevens.
5. Chromite, Coggin mine, Sec. 35, T. 39, N., R. 4. W., Little Castle Creek, Shasta County, California (Stevens, 1944, 7, anal. 9). Analyst, R. E. Stevens.

tural formula was derived. The complete calculations are given in Table 2. The practice of adjusting the iron atoms between RO and R_2O_3 groups so as to give a RO/R_2O_3 ratio of 1:1 (Stevens, 1944, Malhotra and Prasada Rao, 1956) was not followed. It is considered desirable to calculate the structural formula without making any adjustments as this reflects more clearly the variations in the chemical composition of the mineral and the oxidation state of the magma from which it crystallized (Thayer, 1946). Also if all the analyses are recalculated so as to fit the structural formula of the mineral there would be no means of determining accurately the limits of solid solution replacements within this group of minerals.

It will be seen from the structural formula of chromite B-327 (Table 2, No. 1) that the summation of the trivalent group is higher than the

TABLE 2. STRUCTURAL FORMULAE OF THE ZHOB VALLEY CHROMITES

	1			2			
	Wt. %	Mol. Prop.	Cations*	Wt. %	Mol. Prop.	Recal. to .5	Cat-ions
Al_2O_3	9.37	0.0919	2.917	5.28	0.0517	0.0629	2.002
Fe_2O_3	6.16	0.0387	1.227	2.56	0.0160	0.0192	0.604
Cr_2O_3	57.43	0.3777	11.989	52.17	0.3432	0.4172	13.402
V_2O_5	0.04	0.0000	0.000	0.11	0.0006	0.0007	0.002
		0.5083	16.133		0.4115	0.5000	16.000
FeO	9.99	0.1391−.0022[a] =0.1369	2.173	15.30	0.2129−.0025[a] −0.2104	0.2799	4.472
MgO	14.17	0.3514	5.536	13.43	0.3330−.1810[b] =0.1520	0.2022	3.244
MnO	0.38	0.0053	0.084	0.98	0.0124	0.0164	0.261
CaO	0.04	0.0007	0.001	0.06	0.0010	0.0015	0.023
		0.4943	7.794		0.5593−.1835[c] =0.3758	0.5000	16.000
SiO_2	0.80	0.0013		5.44	0.905		
TiO_2	0.18	0.0022		0.20	0.0025		
H_2O+	0.86	0.0040		2.62	0.1459		
RO/R_2O_3		0.99			1.36		
Cr/Fe		3.24			2.88		

* Cations on the basis of 32(0).

[a] Subtracting for ilmenite.

[b] Subtracting for serpentine.

[c] Total subtractions.

Samples 1 & 2 same as in Table 1.

ideal value of 16 and the summation of the bivalent group is correspondingly low. This appears to be due to the oxidation of ferrous to ferric iron. From this it would appear that if the calculations of the structural formulae are made without adjustments, the totals of the trivalent and the bivalent groups can be used as an index of the state of oxidation of chromites. Thayer (1946, 207) has pointed out that FeO/Fe_2O_3 ratio in chromite is a function of the state of the iron in the magma. Since only small amounts of Fe_2O_3 are readily taken into olivine and enstatite structure and the total chromite in the magma is in very minor amounts, slight variations in the Fe_2O_3 content of the magma will be greatly magnified in the FeO/Fe_2O_3 ratios in chromites. It would appear from this suggestion that chromites rich in Fe_2O_3 content were formed under oxidizing conditions.

Thayer (1946, 215) has also pointed out that the chromites rich in Cr_2O_3 occur in feldspar-free peridotites low in alumina, a contention confirmed by the Zhob Valley chromites. This would also account for the low CaO content of chromites. Little is known about the chemistry of the rocks associated with the Zhob Valley chromite deposits, and it is not possible here to comment on the relationship between the chemical composition of these chromites and their host rocks.

Chromites show a wide range of composition due to the isomorphous substitution of FeO by MgO and of Cr_2O_3 by Al_2O_3 and Fe_2O_3. These variations in the chemical composition of chromites can be studied by plotting the composition of unit cells on a triangular prism devised by W. D. Johnson, Jr., and described by Stevens (1944). The six corners of the prism are occupied by $FeO \cdot Cr_2O_3$ (ferrochromite), $FeO \cdot Al_2O_3$ (hercynite), and $FeO \cdot Fe_2O_3$ (magnetite) at the base, and $MgO \cdot Cr_2O_3$ (magnesiochromite), $MgO \cdot Al_2O_3$ (spinel), and $MgO \cdot Fe_2O_3$ (magnesioferrite) at the top. A simpler diagram is the one used by Stevens (1944), where the chemical composition of chromites are plotted on a triangular diagram with $FeO \cdot Fe_2O_3$, $(Mg \cdot Fe)O \cdot Cr_2O_3$ and $(Mg \cdot Fe)O \cdot Al_2O_3$ occupying the three corners of the triangle. By joining the apices of the triangle with the centers of the opposite sides the triangle is divided into six fields. The field in which Cr_2O_3 is the major constituent is the field of chromite, and this has been subdivided into two fields, namely those of ferrian chromite and aluminian chromite, depending upon the second major constituent. The other four fields are of chromian magnetite, chromian spinel, aluminian magnetite, and ferrian spinel.

Figure 2 is a plot of the two new and one old Zhob Valley chromite analyses and the eight Indian chromites described by Malhotra and Prasada Rao (1956). It will be seen from the figure that considerable range of solid solution exists in the chromites, and if the 52 analyses given by Stevens (1944) are also plotted the field of solid solution extends into the upper halves of the chromian spinel and chromian magnetite fields. It will also be noticed that no points fall close to the theoretical chromite ($FeO \cdot Cr_2O_3$), and a review of the published analyses has failed to reveal a chromite close to this composition. Stevens has pointed out that the formula $FeO \cdot Cr_2O_3$ does not adequately represent the chemical composition of natural chromites, and it is here suggested that the chromite formula should be modified to $(Fe, Mg)O \cdot (Cr, Al)_2O_3$. The terms magnesiochromite and ferrochromite suggested by Stevens for chromites rich in magnesium and iron respectively should be more extensively used. It may be added here that Winchell (1956, 82) uses the terms picrochromite and

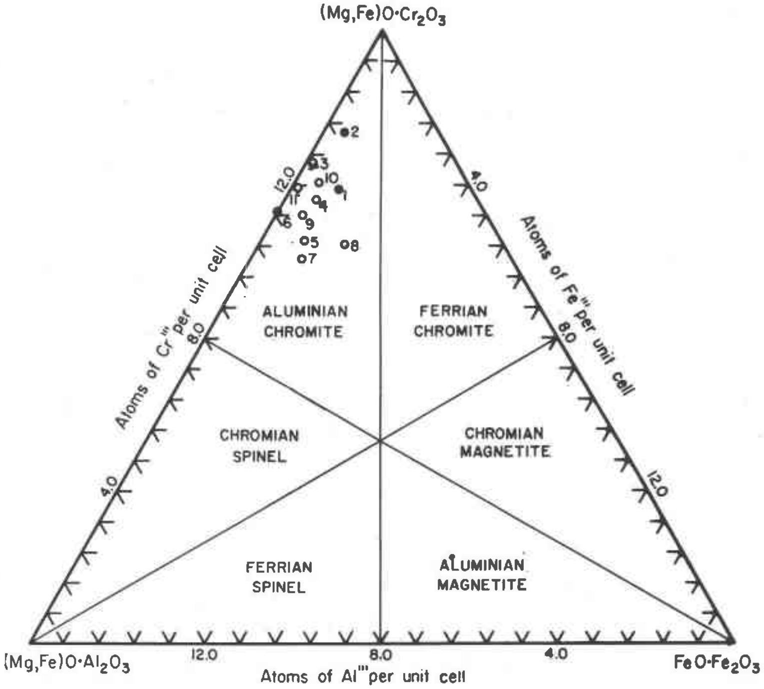

FIG. 2. Triangular diagram showing composition of the Zhob Valley chromites with comparisons. Nos. 1 and 2, new analyses (Table 1, Nos. 1 and 2). Nos. 3–11, same as Nos. 1–8 in Malhotra and Prasada Rao, 1956, 465.

chromite in the same sense as magnesiochromite and ferrochromite of Stevens. The usage of different names for the same mineral causes confusion and should be discouraged. The terms magnesiochromite and ferrochromite have been used here in preference to Winchell's terms because they are more expressive of the composition of the minerals.

Expression of the analyses in terms of end members

The chemical analyses of the Zhob Valley chromites expressed in the forms of end member formula and weight percentages are given in Table 3. The end member formula percentages have been obtained by the following formulae given by Stevens (1944):

$$\text{Spinel} = \frac{\text{Al}}{2}$$

$$\text{Magnesiochromite} = \text{Mg} - \frac{\text{Al}}{2}$$

$$\text{Ferrochromite} = \frac{\text{Cr} + \text{Al}}{2} - \text{Mg}$$

$$\text{Magnetite} = \text{Fe}'' + \text{Mg} - \frac{\text{Cr} + \text{Al}}{2} = \frac{\text{Fe}'''}{2},$$

TABLE 3. END MEMBER FORMULA PERCENTAGES OF CHROMITES (TABLE 1)

	1	2	3	4	5
Spinel	21.9	12.5	23.6	19.9	22.2
Magnesiochromite	39.8	28.0	47.6	51.6	28.9
Ferrochromite	28.9	55.7	24.8	23.4	42.9
Magnetite	9.2	3.8	4.0	5.1	5.9
	End Member Weight Percentages				
Spinel	16.0	8.6	27.3	14.4	10.4
Magnesiochromite	40.9	26.2	42.6	40.6	22.1
Ferrochromite	35.0	60.2	25.8	41.5	63.0
Magnetite	8.1	5.0	4.3	3.5	4.5

where each element is given in atoms per unit cell. The weight percentages have been obtained by multiplying the unit cells by molecular weight and recalculating to 100 per cent.

It will be noticed that the range of composition in the three Zhob Valley chromites (Table 3, Nos. 1–3) is very considerable. Spinel varies from 12.5 to 23.6 per cent, and the variations in the magnesio- and ferrochromites as well as in the total chromite present are fairly large (68.7, 83.7 and 72.4 respectively). There does not appear to be any systematic variation between the end members themselves.

Partial chemical analyses of the Hindubagh-Nasai area chromites are given in Tables 4–6. As a result of this study the chromite occurrences of the area have been divided into three groups depending upon their chemical character and geographical distribution:

1. Chromites of Jungtorgarh group,
2. Chromites of Saplaitorgarh group,
3. Chromites of Nasai group.

TABLE 4. PARTIAL CHEMICAL ANALYSES OF JUNGTORGARH GROUP CHROMITES

S. No.	Mine No.	% Cr_2O_3	% FeO	Cr	Fe	Cr/Fe
1	166B	45.7	11.3	31.2	8.8	3.5:1
2	166C	52.4	12.7	35.8	9.9	3.6:1
3	162A	55.3	14.2	37.8	11.1	3.4:1
4	134	50.8	13.2	34.7	10.3	3.4:1
5	140E	49.4	12.4	33.8	9.8	3.4:1
6	135	41.7	11.3	28.4	8.8	3.2:1
7	203	55.3	13.1	37.8	10.2	3.7:1

Analyst, Shabbir Khan, Pakistan Chrome Mines Ltd., Hindubagh.

TABLE 5. PARTIAL CHEMICAL ANALYSES OF SAPLAITORGARH GROUP CHROMITES

S. No.	Mine No.	% Cr_2O_3	% FeO	Cr	Fe	Cr/Fe
1	7ML[a]	44.6	13.4	30.5	10.4	2.9:1
2	7ML[b]	45.3	14.0	30.9	10.9	2.9:1
3	7ML[c]	48.6	15.2	33.2	11.8	2.9:1
4	136	43.9	12.7	30.0	9.9	3.0:1
5	3AML/6	44.0	12.9	30.1	10.1	3.0:1
6	23A	47.1	13.8	32.2	10.8	2.9:1
7	34	42.6	11.9	29.1	9.4	3.0:1
8	186	52.5	15.9	39.9	12.4	2.9:1

Analyst, Shabbir Khan.

[a,b,c] Samples from surface, 25 feet and 40 feet below surface, respectively.

1. *Chromites of Jungtorgarh group*

Jungtorgarh is the highest hill composed of ultra basic rocks (in the Zhob Valley). It occupies about 20 square miles area and is over 9600 feet above the sea level. The dominant rock type in the hill is harzburgite (olivine enstatite rock). Chromite occurs in harzburgite in veins, bands and lenses. Globules are common, and the deposits do not show any definite shape or size. About thirty mines are being worked in this group. It is not possible to give any idea of the size of these deposits as ore reserves have not been determined, but some of the mines have produced as much as 18,000 tons of high-grade ore (Cr_2O_3 content above 48 per cent), and are still shallow workings.

Chemically the chromites of Jungtorgarh are characterized by high Cr/Fe ratio and this applies even to low-grade ores. It will be noted from the partial analyses in Table 4 that all the samples show a Cr/Fe ratio greater than 3:1.

TABLE 6. PARTIAL CHEMICAL ANALYSES OF NASAI GROUP CHROMITES

S. No.	Mine No.	% Cr_2O_3	% FeO	Cr	Fe	Cr/Fe
1	153[a]	46.3	14.9	31.6	11.6	2.7:1
2	153[b]	53.8	17.6	36.2	13.7	2.7:1
3	2CPL	44.1	14.8	30.1	11.5	2.6:1
4	1CPL	39.5	12.4	27.0	9.8	2.7:1
5	3CPL	41.1	12.2	28.1	10.3	2.7:1
6	34M1	35.6	11.3	24.3	8.8	2.8:1
7	2CPL/1	39.6	13.8	27.1	10.8	2.5:1

Analyst, Shabbir Khan.

[a,b] Samples from 31 and 72 feet below the surface, respectively.

2. *Chromites of Saplaitorgarh group*

This is one of the largest hills in the Zhob Valley and occupies an area of over 90 square miles. There are over 40 mines being worked in this hill, but like Jungtorgarh the deposits in this hill also show no definite shape, size or form. Many of the deposits are low-grade at the surface but improve in depth. The enrichment in Cr_2O_3 content does not lead to an improvement in the Cr/Fe ratio. It can be stated that as a general rule the ratio does not vary substantially within the same deposit (Table 5, anal. 1–3). It will be noticed that chromites from this group show a very variable Cr_2O_3 content but the Cr/Fe ratio almost invariably shows a close approach to the theoretical ratio of 3:1.

3. *Chromites of Nasai group*

The third group is situated at a distance of 20 miles from Hindubagh, but the mines occur in almost a continuous belt from Hindubagh to Nasai. Here also the deposits vary in shape and size but are usually larger than in the other two groups. Most of the deposits in this group are low-grade at the surface but improve in depth. Over 80 mines are being worked in this group and some of these have produced as much as 35,000 tons of chromite and are still shallow workings. Partial chemical analyses of seven samples from this group are given in Table 6. It will be noticed that all the samples show a Cr/Fe ratio smaller than 3:1. This holds both in the case of low- as well as high-grade ores.

GENERAL DISCUSSION

It is not safe to draw conclusions from such scanty data as are available at the moment, particularly when the area under discussion is so large. A few suggestions, however, are made here tentatively regarding the petrogenetic significance of the analyses given above. It is a well known fact that in the crystallization of basaltic magmas the minerals to crystallize first are rich in magnesium and low in iron. Less is known about the behavior of chromium but chromite is generally regarded as an early crystallization product. With the continued crystallization the magma becomes richer in iron and poorer in magnesium and chromium; thus the minerals crystallizing in the later stages are enriched in iron. From the above remark it can be inferred that those of the chromites which show a high Cr/Fe ratio are earlier in age than those showing a lower ratio. Age relationships between the rocks of the Zhob Valley igneous complex are not known, and a great deal of research is needed before the petrogenesis of the various rock types (including the chromite deposits) can be worked out. Further work on this problem is in progress and the results will be presented at a later date.

METHOD OF CHEMICAL ANALYSIS OF CHROMITE

Preparation of the sample

The material for analysis is ground to pass a 325 mesh screen. The fine grinding does not appear to result in excessive oxidation of ferrous iron (Seil, 1943), especially if the grinding is done by hand and the sample is screened frequently to avoid doing excessive work on the fines. The sample should be thoroughly mixed and it may be desirable to air dry the powder before mixing by spreading it in a thin layer on a glazed paper overnight.

It should be noted that excessive amounts of certain impurities, for example silicate minerals, may lead to difficulties, particularly in the determination of ferrous iron by the indirect method described.

Determination of water

Water is determined by Penfield method, using lead oxide (PbO) as a flux. A moisture determination is hardly worthwhile as a rule, for it has been shown (Hartford, 1953), that a temperature of 200° C. or higher may be necessary to remove moisture from such samples, and there is a danger of oxidation of ferrous iron at this temperature. Also, silicate minerals present as impurities will probably contain chemically combined water, so that total water determination must be made in any case.

Determination of ferrous iron

The most reliable methods for the determination of ferrous iron in chromite are the closed tube (Mitscherlich) method and the indirect method of Seil (1943). Modifications of the latter have been devised, and these have been well summarized and discussed by Dinnin (1959). The essentials of the closed tube method have been described by Hillebrand (1953). In the present work the original procedure of Seil, slightly modified is used. The apparatus is illustrated in Fig. 3 and some comparative results are given in Table 7.

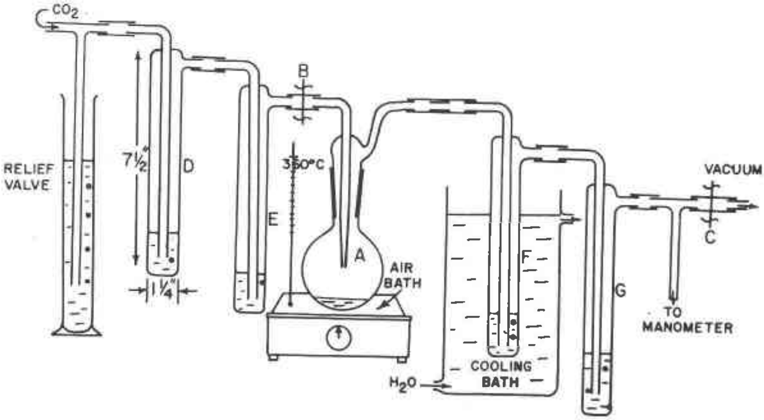

FIG. 3. Apparatus for ferrous iron determination. (A) Standard 200 ml. round-bottom Pyrex flask. (B, C) Pinch clamps to control gas flow. (D) Bubbler containing 6 per cent sodium bicarbonate solution to which has been added slightly less than an equivalent amount of ferrous ammonium sulfate, to remove O_2 and H_2S from the carbon dioxide. (E) Washing bubbler containing water. (F, G) Bubblers containing standard dichromate in 5 per cent sulfuric acid. All connections are made with heavy-wall Tygon tubing.

TABLE 7. COMPARISON OF FERROUS IRON DETERMINATION RESULTS BY VARIOUS METHODS

Sample	Per cent FeO	
	Seil's method	Others
Chromite	11.29	11.35[1]
Chromite	21.25	21.32[1]
Chromite	21.40	21.42[1]
Biotite	20.95	20.61[2]
Ferrous ammonium sulfate	18.24	18.32[3]

[1] Closed tube method, R. B. Ellestad, analyst.
[2] Solution in HF-H_2SO_4, permanganate titration.
[3] Theoretical value.

Procedure

To the two bubbler tubes F and G (Fig. 3) add 20 and 2 ml. (more or less, depending upon the ferrous iron expected) respectively of 0.1 *N* potassium dichromate in 5% (v/v) sulfuric acid. Make up the volume in each tube to about 20–25 ml. with 5% sulfuric acid. To the reaction flask (previously filled with carbon dioxide if there is any danger of reaction between the wet sample and the air, as for example with ferrous ammonium sulfate used in standardizing and checking the procedure) add the sample, using a paper cylinder or other device to prevent it from sticking to the neck of the flask. Usually 0.5 gm. sample is used for chromite. Add 25 ml. of acid mixture (H_3PO_4:H_2SO_4::4:1). Lubricate the ground glass joint with syrupy phosphoric acid, and assemble the apparatus as shown in Fig. 3.

Evacuate slowly, start a slow current of carbon dioxide (1 bubble per second in the dichromate bubblers) and turn on the hot plate. Heat slowly until all water is boiled off, and finally hold the temperature of the air bath at 360° C. until reaction stops, and for 20 minutes thereafter. Overheating must be avoided, particularly if silicate impurities are present. Clamp the suction line, and allow carbon dioxide to enter the apparatus slowly until it is at atmospheric pressure. Disconnect the dichromate bubblers, and wash their contents into a conical flask, using freshly boiled and cooled water. Displace the air with carbon dioxide, add approximately 4 grams of potassium iodide and 10 ml. of 1:1 sulfuric acid, wash down the sides of the flask with boiled water, cover, and allow to stand in dark for 5 to 10 minutes. Titrate with N/10 sodium thiosulfate solution, adding starch indicator as the end point is approached.

Run a blank determination on the reagents, and correct the titration accordingly. It is advisable to determine ferrous iron in a known material (ferrous ammonium sulfate serves well if it has been assayed for ferrous iron content by direct titration with dichromate) to be sure that the carbon dioxide is free from oxygen. Reserve the solution of the sample for the determination of chromium.

Determination of manganese and vanadium

Manganese and vanadium are conveniently determined on the same sample after fusion with peroxide and leaching the melt with water. Manganese remains in the insoluble residue and vanadium is determined in the filtrate.

Procedure

Fuse 0.5 gm. of sample with 5 gm. of peroxide in an iron crucible until a quiet melt is obtained. Cool, leach with water, add a little peroxide, boil for 1–2 minutes, and digest on the steam bath for 1 hour or until all peroxide is decomposed. Cool, and allow to stand overnight. Filter through a hardened paper (Whatman No. 41H) folded inside a retentive one such as S and S Blue ribbon. Wash thoroughly with dilute sodium hydroxide solution containing a little carbonate. Manganese is determined in the residue after solution in nitric acid by standard colorimetric procedures.

To the filtrate add water and sulfuric acid to give 300–400 ml. of solution containing 5% (v/v) of sulfuric acid. Add excess peroxide to reduce chromium, and boil to remove excess. Precipitate vanadium with cupferron as described by Schoeller and Powell (1955). Burn off the paper and precipitate at low temperature, fuse the residue with a little pyrosulfate, take up with water, and determine vanadium colorimetrically as peroxyvanadate (Sandell, 1959).

Determination of silica, alumina, titania, iron, calcium and magnesium oxides

The main portion of the analysis follows traditional lines, but is complicated by the presence of large amounts of chromium. To avoid the introduction of platinum into the analysis, a wet attack using perchloric acid is favored. This results in the oxidation of chromium, which then remains for the most part in solution throughout the analysis. Nevertheless it is not possible to prevent the separation of a small part of the chromium with the ammonia group of elements, and manganese, which normally escapes precipitation with ammonia, is almost completely thrown down. Thus to obtain a figure for alumina, it is necessary to subtract from the ammonia group not only iron and titania, but chromium, vanadium, and manganese oxides as well.

Since chromites seldom contain appreciable amounts of calcium, the oxalate precipitation which normally follows the ammonia precipitation is omitted, and calcium is allowed to coprecipitate as phosphate with the magnesium. In the absence of oxalate, nickel may be completely precipitated with magnesium, and should therefore be looked for, along with calcium and manganese in the $Mg_2P_2O_7$.

Procedure

Weight 0.7 gm. of sample into a 400 ml. beaker and add a little nitric acid and 50 ml. of concentrated perchloric acid. Cover, and place a stirring rod in the beaker spout, tangent to the bottom of the cover and touching opposite side of the beaker so that acid condensing on the cover will run freely back into the solution without condensing in drops. Heat on a plate, gently first but gradually increasing the heat until the sample is all in solution, the chromium is all oxidized, and the acid shows itself to be constant boiling by the fact that no spatter occurs when the condensate runs back into the solution. Continue boiling for 20 minutes after the stage is reached.

Cool the mixture rapidly, add 50 ml. of water, stir, and boil for 1–2 minutes. Add 100 ml. of cold water and filter at once through a paper which has been washed with 25% perchloric acid. Scrub the beaker, transfer all the residue to the filter, and wash well with 2 per cent perchloric acid and then with hot water. Ignite to constant weight, and determine SiO_2 as usual by volatilization with hydrofluoric acid. Fuse the residue with a little sodium carbonate, and add it to the main solution.

Heat to boiling, and precipitate with ammonia at pH 6.5–7.0 in the usual manner. Filter through a double paper and wash with 2 per cent ammonium nitrate solution. Return the precipitate to the beaker, keeping the paper intact. Add 10 ml. of nitric acid and heat gently. When solution is complete, dilute to 150–200 ml., boil for a few minutes, add about 5 ml. in excess of ammonia and 1 drop of 30 per cent hydrogen peroxide. Boil for 10 minutes to destroy peroxide, make just acid with nitric acid, and then adjust the pH to 7.0 with ammonia. Heat to boiling and filter through the same paper as before.

Repeat the precipitation a third time, macerating the inner paper and stirring just before filtering through the original outer paper. It is advisable to catch the three filtrates in separate beakers so that the progress of separation of the chromium may be followed. If the third filtrate is still highly colored, a fourth precipitation should be considered.

Ignite and weigh the ammonia group oxides. Fuse the precipitate with pyrosulfate, leach with water containing 3–5 ml. of sulfuric acid, and evaporate or dilute to about 80 ml. Add strong (50%) sodium hydroxide solution until the precipitating iron hydroxide redissolves on stirring only with difficulty. Heat 200 ml. of 5% sodium hydroxide to boiling in a 400 or 600 ml. beaker. Add 1 ml. of 30 per cent hydrogen peroxide to the nearly neutralized solution of the oxides, and pour quickly into the hot alkali solution. Cover at once to prevent loss by spattering, then wash the contents of one beaker into the other completely. Heat to boiling, and digest the alkaline solution on the steam bath for two hours or more to decompose peroxide completely, stirring from time to time. Cool, stand overnight, and filter through a hardened paper (Whatman No. 41H) fitted inside a retentive one (S and S Blue ribbon). Wash throughly with 2 per cent sodium hydroxide containing a little sulfate and carbonate, and finally once or twice with water to remove some of the alkali salts.

Determine chromium in the filtrate, either colorimetrically or titrimetrically with iodide and thiosulfate. If vanadium is not determined on a separate sample, it may be separated at this stage with cupferron after the chromium determination.

A small amount of iron always escapes precipitation by sodium hydroxide, or finds its way in colloidal form through the tightest filter. This may be separated with the vanadium and determined colorimetrically with *o*-phenanthroline, or the alkaline filtrate may be evaporated to small volume, then diluted and filtered through a pulp filter, when the small amount of iron so recovered can be added to the main sodium hydroxide precipitate. The latter procedure is necessary if the chromium is to be determined colorimetrically as chromate.

Wash the sodium hydroxide precipitate, which contains the iron and titanium, into the precipitation beaker, transfer the paper to a platinum crucible, and ignite. Fuse the small residue with pyrosulfate, leach with water, and add the solution to the main one. Adjust to 5 per cent sulfuric acid, add peroxide, and determine titanium colorimetrically, reserving all the solution for the determination of iron.

After the titanium determination, heat the solution to decompose peroxide, evaporate to about 50 ml., and precipitate platinum with hydrogen sulfide. Filter, and wash with dilute sulfuric acid. Boil off hydrogen sulfide, and evaporate the solution to about 50–75 ml. Add 20 ml. of concentrated hydrochloric acid, and reduce the iron with a slight excess of stannous chloride. Titrate potentiometrically with potassium dichromate.

Precipitate magnesium (manganese, calcium, nickel) in the filtrate from the ammonia group precipitate by adding 10 grams of diammonium phosphate and making the solution 10 per cent in ammonia. After 48 hours, filter, wash with 5 per cent ammonia, dissolve the precipitate, and reprecipitate. Ignite and weight $Mg_2P_2O_7$. Dissolve the pyrophosphate in sulfuric acid and precipitate calcium in 80 per cent alcohol solution. Filter, wash with 80 per cent alcohol, and dissolve the calcium sulfate in dilute hydrochloric acid. Determine calcium either gravimetrically after precipitation as oxalate or titrimetrically with versene. In correcting the magnesium figure, assume calcium present as $Ca_3(PO_4)_2$.

Evaporate the alcoholic filtrate from the calcium sulfate to fumes of sulfuric acid, dilute with water, and filter. Aliquot the solution and determine manganese colorimetrically after periodate oxidation, and nickel gravimetrically after precipitation with dimethylglyoxime. Assume that manganese and nickel were weighed as pyrophosphates with the magnesium and make suitable corrections.

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