

A microprobe study of chromites from the Andızlık-Zımparalık area, south-west Turkey

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SUMMARY. Compositional changes in chromites are shown to be related to the degree of alteration of the grains to 'ferritchromit'. The chromium content of late stage pyroxenites and tremolites may be related to the development of the 'ferritchromit'. Analysed grains from the chrome ores are shown to have a different chemistry to the accessory chromites in the peridotites.

THE peridotites of south-west Turkey can be divided into northern and southern units. They extend eastwards from the Datça peninsula, each unit covering an area of over 700 km² (fig. 1). General accounts of these two units have been given by Kaaden and Metz (1954), Kaaden (1959, 1960), Altınlı (1955), Colin (1962), Graciansky (1968), and Engin (1969).

The Andızlık-Zımparalık area is situated at the eastern end of the northern peridotite unit, 40 km north of Fethiye (fig. 1). This area is an economic source of chrome ore. The peridotite body has a general trend north-west-south-east. The contacts with the surrounding sedimentary rocks in the south and in the north are marked by thrust zones dipping towards the peridotite. The sediments are unmetamorphosed, and mainly comprise Palaeozoic and Mesozoic limestones and Miocene flysch.

The peridotite is mainly harzburgite, which consists of forsteritic olivine, orthopyroxene, and serpentine with minor amounts of clinopyroxene and chromite. On average, the peridotite is over 50% serpentinized (Engin and Hirst, in preparation). The peridotite contains intrusive basic dykes, which form about 10% of the mass. Orthopyroxenite and tremolite veins associated with chromite cut the peridotite and are common in the area.

Chromite deposits are known throughout the peridotite and are of podiform type (Thayer, 1964; Engin, 1969). Lenticular-shaped chromite bodies are known, up to 50 m long and 8 m thick. The chromite bodies usually have sharp contacts with the host peridotite; slickensides are commonly observed at these contacts suggesting that the chromites and peridotites are not genetically related in their present position, the chromites and peridotites having moved differentially during tectonic movements, probably associated with the Alpine orogeny.

Detailed work on the Andızlık-Zımparalık area indicates that a limited amount of chromium may have been transported by hydrothermal solutions. Whole rock

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analyses of harzburgites, pyroxenites, and tremolites show that the chromium contents of the pyroxenites and tremolites are higher than those of the harzburgites although the harzburgites contain more chromite. It is thought that the orthopyroxenites and tremolites are late stage veins generated by hydrothermal activity. To confirm these analyses the chromite contents of one orthopyroxenite and three tremolite specimens have been separated and the samples analysed on a chromite-free basis. The chromium contents were still higher in the pyroxenites and tremolites than in the host harzburgites. Therefore it has been concluded that during hydrothermal activity a limited amount of chromium was probably removed from the chromite bodies and taken into the pyroxene and tremolite structures.

'Ferritchromit' development. During the episcopic study of the chromites, light-coloured areas with a higher reflectivity than the host chromite were observed along fractures within the grains and along some of the chromite margins. As these areas were about $1\ \mu\text{m}$ in size reflectivity measurements were unsuccessful. Similar features have been described by Horninger (1941), Wijkerslooth (1943), Spangenberg (1943), Amin (1948), Maxwell (1949), Den Tex (1955), Panagos and Otteman (1966), Golding and Bayliss (1968), Mihalik and Saager (1968), and Beeson and Jackson (1969). Horninger terms this material 'ash coloured magnetite' and Spangenberg gave it the name 'ferritchromit'. Wijkerslooth (1943), Horninger (1941), and Spangenberg (1943) have attempted to explain the development of 'ferritchromit' by hydrothermal resorption commencing along fine cracks in the chromite. During this process, Al_2O_3 and MgO are removed from the chromite and added to the surrounding serpentine, changing it into chlorite or tremolite. Alternatively hydrothermal solutions from the serpentine may have caused the removal of Fe.

In the chloritic chromites from Australia, Golding and Bayliss (1968) have shown that 'ferritchromit' zones are higher in Cr_2O_3 and FeO but lower in Al_2O_3 and MgO than the host chromite. They say that alteration of chromite involves the oxidation of primary chromite and concomitant chloritization of associated serpentine, olivine, and pyroxene. Oxidation was presumably initiated at lattice defects within

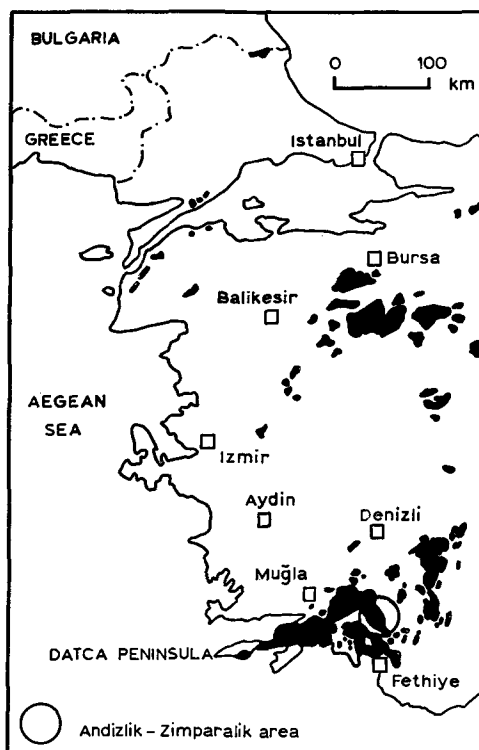


FIG. 1. Location of the Andızlık-Zımparalık area, western Turkey. The mafic and ultramafic rocks are shown black.

micro-fissures above some threshold of oxygen activity controlled by the physical and chemical nature of the vapours penetrating the ore.

Beeson and Jackson (1969) have shown that in the altered parts of the chromites from the Stillwater complex Al_2O_3 abruptly decreases and FeO and Cr_2O_3 abruptly increase; replacement of Mg by Fe^{2+} in the spinel lattice precedes that of Al by Fe^{3+} . They came to the conclusion that position, bonding, and ionic size are not the controlling factors in the mobility of Mg or Al in the lattice, but rather that the availability of Fe^{2+} or Fe^{3+} fixes the amount of Mg and Al that are replaced.

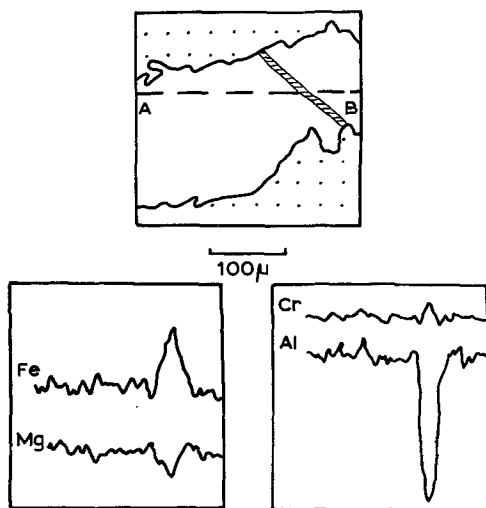


FIG. 2. Sample F47.1, electron-probe scan along the line A-B. Ferritchromit zone is lined, serpentine dotted, and chromite unshaded.

(fig. 2) that Cr and Fe are higher in the 'ferritchromit' but Al and Mg lower when compared with the host chromite.

In order to study the compositional changes in the chromites quantitatively, 64 spots from three chrome ores (F31, F115, F47) and accessory chromite from three harzburgites (F29, F44, F251) have been analysed by electron probe. The results are given in table I. The position of the analysed spots within the chromite grains from the chrome ores are shown in fig. 3.

The standards used for the analyses were chromium metal, synthetic Fe_2O_3 , and synthetic enstatite with 10% Al_2O_3 (for Mg and Al). Peak counts were adjusted for background, dead time, and drift by means of a computer program written by one of us (J. W. A) specifically for Geoscan electron-probe output. The output from this program was then corrected for absorption, fluorescence, and atomic number effects. The corrections are those proposed by J. V. P. Long (University of Cambridge, private publication) and were made by a computer program written by T. Patfield (University of Leeds, private communication).

Describing 'ferritchromit' rims in nodular chromite from Rodiani, Greece, Panagos and Otteman (1966) give cell-edge of the host chromite as 8.24 \AA and 'ferritchromit' as 8.34 \AA . Mihálik and Saager (1968, table I, p. 1548) in a study of Witwatersrand placer chromite grains gave reflectivity and microhardness values for the host chromite and altered chromite ('ferritchromit'); the former is the harder of the two.

Electron microprobe analyses were made on a twin-channel Geoscan electron microprobe with a take-off angle of 75° . Scans and spot counts were made for the elements Cr , Al , Fe , and Mg on 'ferritchromit' material and normal chromites from the Andızlık-Zımparalık area. The scans show

TABLE I. Electron microprobe spot analyses

<i>Chromites from chrome ore</i>											
	F47.11	F47.12	F47.13	F47.14	F47.15	F47.16	F47.17	F47.18	F47.19	F47.110	F47.21
Cr ₂ O ₃	56.48	57.02	62.59	63.56	62.04	61.92	56.33	57.88	55.84	56.21	56.75
Al ₂ O ₃	12.78	12.87	3.24	1.27	2.81	2.66	12.68	13.17	13.92	12.60	12.76
FeO*	17.93	17.78	23.92	26.04	28.13	28.14	18.34	18.57	18.11	18.56	17.48
MgO	12.81	12.33	10.25	9.13	7.02	7.29	12.65	10.38	12.13	12.63	13.00
	F47.22	F47.23	F47.24	F47.25	F47.26	F47.27	F47.28	F47.29	F115.11	F115.12	F115.13
Cr ₂ O ₃	57.51	53.82	56.80	57.23	57.36	57.57	57.13	56.29	54.59	54.53	54.31
Al ₂ O ₃	13.25	12.39	12.88	12.78	12.65	12.85	12.95	14.34	14.65	14.55	14.55
FeO*	16.88	21.26	17.46	17.09	16.98	16.84	17.10	21.80	16.99	17.00	17.13
MgO	12.36	12.52	12.86	12.90	13.01	12.73	12.82	7.56	13.78	13.92	14.00
	F115.14	F115.15	F115.16	F115.17	F115.21	F115.22	F115.23	F115.24	F115.25	F115.26	F31.11
Cr ₂ O ₃	48.34	54.14	54.17	53.97	54.63	53.71	54.28	54.79	51.74	54.40	60.37
Al ₂ O ₃	15.02	14.60	9.22	8.12	13.97	14.73	14.02	13.15	9.73	9.27	11.39
FeO*	28.31	18.12	28.43	28.93	21.40	19.04	20.03	21.51	29.04	27.62	14.50
MgO	8.33	13.13	8.18	8.98	10.00	12.52	11.67	10.55	9.48	8.72	13.74
	F31.12	F31.13	F31.14	F31.15	F31.16	F31.17	F31.18	F31.19	F31.110	F31.111	
Cr ₂ O ₃	59.28	59.48	58.77	58.25	58.28	60.65	58.59	58.27	58.31	58.54	
Al ₂ O ₃	11.59	12.24	11.28	11.82	11.90	10.03	11.36	11.48	11.66	11.66	
FeO*	15.30	14.72	15.72	15.27	15.10	15.80	15.68	15.66	15.13	15.09	
MgO	13.82	13.56	14.23	14.66	14.72	13.52	14.36	14.60	14.91	14.71	
<i>Accessory chromites from harzburgites</i>											
	F44.11	F44.12	F44.13	F44.14	F44.21	F44.22	F44.23	F44.24	F44.25	F251.11	F251.12
Cr ₂ O ₃	46.26	45.83	42.46	42.92	44.86	44.13	46.77	46.50	44.44	51.01	51.85
Al ₂ O ₃	22.57	23.07	25.39	25.30	23.86	24.17	22.63	22.53	23.87	18.18	17.32
FeO*	19.44	19.46	20.24	18.90	18.71	18.67	18.37	18.80	19.56	19.06	18.93
MgO	11.72	11.65	11.91	12.88	12.58	13.02	12.22	12.17	12.13	11.75	11.90
	F251.13	F251.14	F251.21	F251.22	F251.23	F29.11	F29.12	F29.13	F29.21	F29.22	
Cr ₂ O ₃	51.32	51.26	50.00	51.60	48.86	44.85	46.65	44.81	42.50	47.13	
Al ₂ O ₃	17.90	17.61	19.06	17.80	19.50	22.23	21.00	22.41	24.37	20.19	
FeO*	19.15	19.89	19.67	19.16	20.04	21.59	21.32	21.24	21.03	21.75	
MgO	11.63	11.23	11.27	11.45	11.60	11.33	11.03	11.54	12.10	10.92	

* Total iron as FeO.

Analysed spots 3, 4, 5, and 6 in grain F47.1 (fig. 3) are from a 'ferritchromit' zone. The analyses (table 1) confirm that this material is lower in Al_2O_3 and MgO but higher in total iron (expressed as FeO) and Cr_2O_3 than the associated host chromite.

Analyses of spots in specimen F115 can be placed into two groups, F115.1 spots 4, 6, 7 and F115.2 spots 5, 6 (fig. 3) constitute one group, and are distinct from the remainder.

They are generally lower in MgO and Al_2O_3 and higher in total iron; the differences in Cr_2O_3 are insignificant. Normal episcopic examination fails to reveal these differences but in this example they may be resolved by measurements of the reflectivity. No significant changes in composition were detected in the analyses of sample F31 (fig. 3).

The electron-probe results indicate that changes in composition in F115 are similar to the changes leading to the formation of the 'ferritchromit' of F47. This suggests that the compositional variation may be a result of hydrothermal activity. The compositional changes are not however as extreme as in the formation of the 'ferritchromit'.

Analyses from the accessory chromites F29, F44, and F251 show slight chemical changes within each sample (table I and fig. 5). The margins of the accessory grains have a lower

$\text{Cr}_2\text{O}_3/\text{FeO}$ ratio and higher $\text{Al}_2\text{O}_3/\text{MgO}$ ratio than the cores. It is difficult to decide whether the variation is due to hydrothermal effects or fractionation during crystallization of the harzburgites. The latter process is possible, as the silicate matrix of specimen F251 is not altered to serpentine or chlorite while normal alteration of chromite to 'ferritchromit' produces a lower $\text{Al}_2\text{O}_3/\text{MgO}$ ratio, not a higher ratio as is the case here.

All the analyses have been plotted on a Cr_2O_3 - Al_2O_3 -(MgO+FeO) triangular diagram (fig. 4). The four distinct groups of analyses are clearly seen, being divided into unaltered chromites from the chrome ores, 'Ferritchromit', slightly altered chrome-ore chromites, and accessory chromites in harzburgites.

Chemical differences between the unaltered chromites from chrome ores and the accessory chromites in harzburgite are distinct, but present a continuous variation. Accessory chromites are richer in Al_2O_3 but poorer in Cr_2O_3 . This is certainly related to the crystallization sequence and position within the magma chamber. The chrome ores were the early phases to crystallize followed by accessory chromites associated

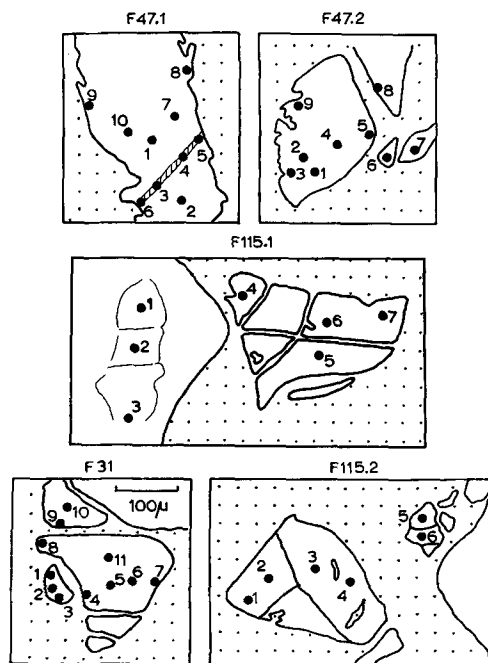


FIG. 3. Position of analysed spots in chrome ores, chromite is unshaded, 'ferritchromit' lined, and serpentine dotted except in F115 where it is chlorite.

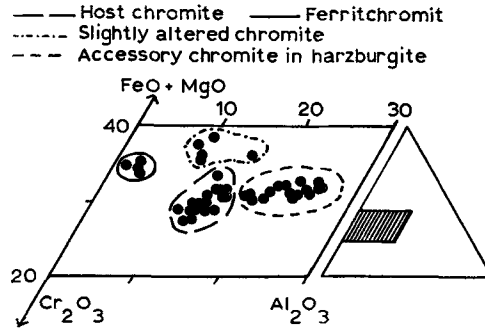


FIG. 4. Relationship between the accessory chromites of the harzburgite, host chromite, and 'ferritchromite' zones in the system $Al_2O_3-Cr_2O_3-(FeO+MgO)$.

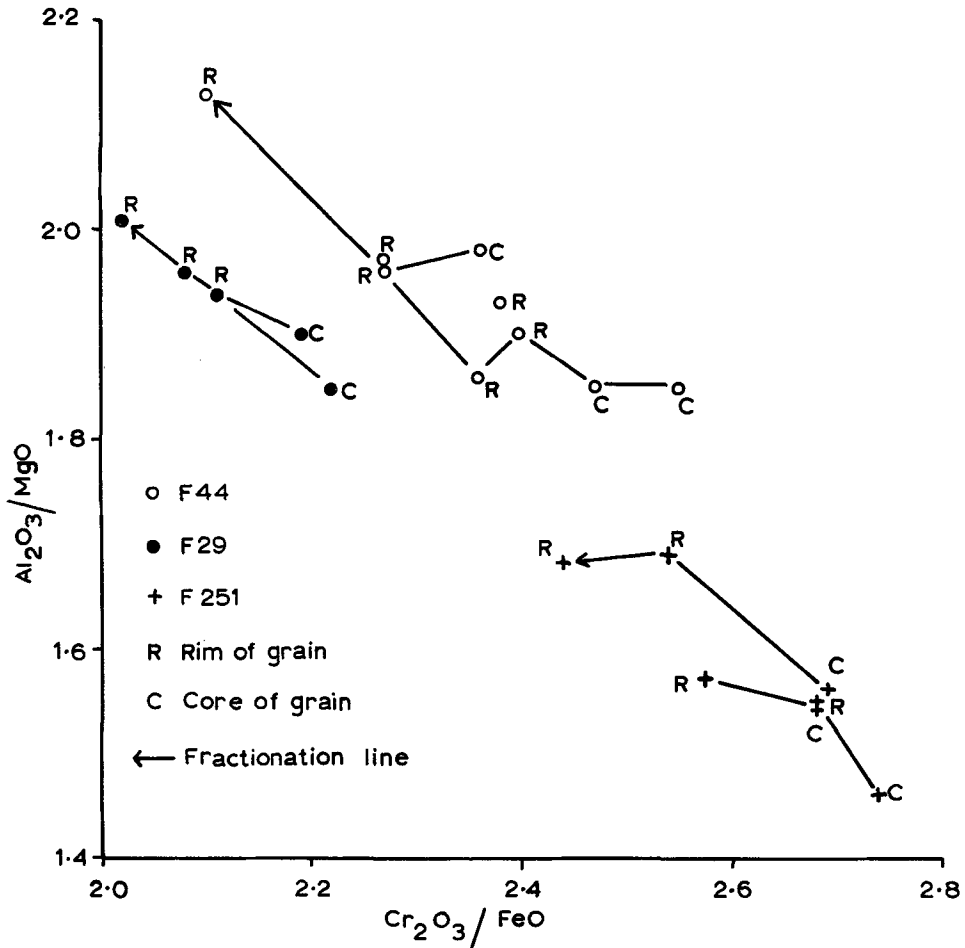


FIG. 5. Variation of the Cr_2O_3/FeO and Al_2O_3/MgO ratios between the rims and cores of the accessory chromites in the harzburgite.

with the harzburgites at a structurally higher level within the magma chamber or a higher level in the crust. The chromite ore bodies were then tectonically emplaced into the upper parts of the intrusion, hence earlier chrome-rich chromites are associated with the surrounding harzburgites containing the chrome-poor accessory chromites.

The development of the 'ferritchromit' zones in the chromite grains is believed to be the result of hydrothermal activity. If the pyroxenite veins and chromium-bearing tremolites were formed by the same hydrothermal solutions, it is difficult to envisage the Cr being supplied from chromite, since there is slight enrichment of Cr in the 'ferritchromit'.

During the development of 'ferritchromit', Al_2O_3 and MgO have been removed preferentially from chromites, leaving behind zones enriched in Cr_2O_3 and FeO. This suggests that Cr is not easily removed from the chromite by hydrothermal solutions, and this may have some bearing on the source of Cr in the tremolite and pyroxenites. If no Cr is leached from the chromites during the formation of the 'ferritchromit' zones then it is probable that the chrome tremolite and pyroxenites were formed during a separate hydrothermal phase. If on the other hand, Al_2O_3 , MgO, and Cr_2O_3 are leached during the formation of the 'ferritchromit' but chromium is leached at a slower rate, the resultant would be an apparent enrichment of Cr_2O_3 in relation to Al_2O_3 and MgO. Hence the formation of chrome tremolite, pyroxenite, and the 'ferritchromit' zones could be contemporaneous.

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