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Zoned Mn-rich chromite from podiform type chromite ore in serpentinites of northern Greece

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Abstract

Magnetite–chromite ore occurs as small lenses or dikes at the peripheral parts of serpentinites of northern Greece. Cores of chromite are surrounded by small zones of ferrit-chromit and rims of magnetite. Electron microprobe study across zoned chromite grains shows compositional variation ranges unknown to date in spinel minerals. Cr, Al and Mg decrease as Fe and Ni increase outward from the core; Mn increases gradually outwards and attains its greatest values (up to 14.4 wt.%, MnO) in the periphery of chromite cores and in the ferrit-chromit, and drops off to zero in the magnetite rim.

There is an asymmetry of the Mn peaks across the zoned chromite grains with an asymmetrical magnetite rim. The increase of Mn content proportional to the magnetite rim and a manganese balance in the zoned chromite suggest that the trend of the increasing Mn content is related to the progressive metasomatism of the chromite. The high Mn content in the enrichment zone is probably due to substitution of Mn for Mg and in part for Fe^{2+}, the Mn deriving from chromite already transformed to magnetite.

Introduction

Chromite ore is found accompanying serpentinites of the Vermion, Olympus and Edessa regions of northern Greece (Fig. 1). These rocks at the boundary of Pelagonian and Almopias zone are frequently overlain unconformably by Upper Cretaceous conglomerates, limestones, and Eocene flysch (Brunn, 1960; Godfriaux, 1964; Mercier, 1966a, 1966b).

The chromite ore is found at the contact of the serpentinites with the sedimentary rocks as well as within the serpentinite itself, in the form of lenses and dikes (4 m thick) in the Vermion region and as small lenses in the Olympus and Edessa regions. These occurrences are relatively small and range from 0.2 m to 2.0 m in width and from 0.5 m to 50 m in length.

The ore consists mainly of magnetite with minor cores of chromite. It is suggested that a pre-existent chromite ore subsequently transformed to ferrit-chromit and magnetite in variable proportions. The ratio of magnetite to chromite ranges from 0.2 to 9.0. The highest magnetite values are seen in deformed, fine-grained ore. The periphery of chromite core and an intermediate zone of ferrit-chromit contain up to 14.4 wt.% MnO. From a perusal of the literature it is concluded that no comparably zoned chromites have been previously described.

Mineralogy

The main mineral of the ore is magnetite. The chromite is minor and in most cases occurs as magnetite cores. Sulfide minerals are present in small amounts with millerite the most abundant; chalcopyrite and pyrite are very minor. Abundant silicate minerals (garnets, idocrase, chlorite serpentine and talc) are also present (Economou, 1979).

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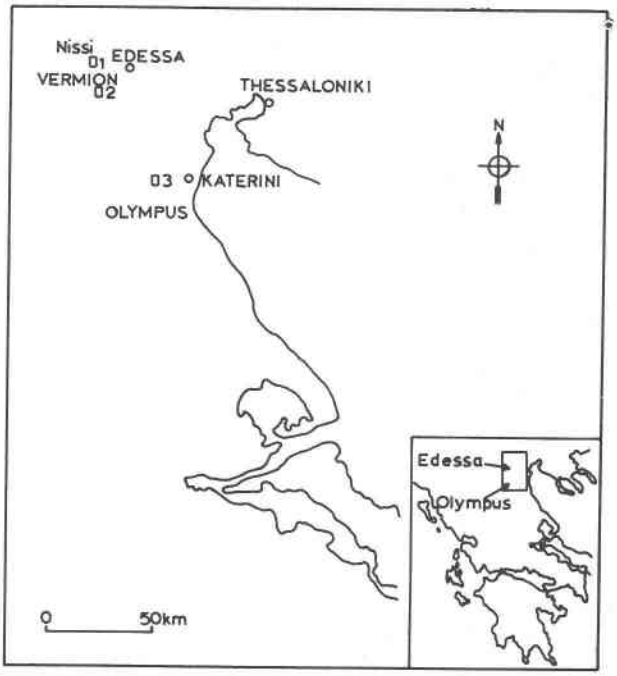

Fig. 1. Sketch map of northern Greece, showing the localities of magnetite–chromite ore deposits studied. 1–Nissi area of Edessa region; 2–Stournari, Kria Vrissi and Mavrolivado area of Vermion region; and 3—Paliabela area of Olympus region.

The chromite cores are isotropic: in reflected light they are brownish grey whereas the magnetite rim is light grey. The mean of microhardness is 1010 VHN. X-ray study shows the mineral to have the cubic spinel structure.

Analytical procedures

Microprobe analyses were made at Manchester University by a Link Systems Model 290-2kx energy dispersive spectrometer, attached to a Cambridge Instruments Geoscan. All analyses were made using 100 second counting times. The spectra were processed using a commercial version of the program developed by Statham in Dr. J.V.P. Long's laboratory in Cambridge. Pure metal for Mn and Fe and synthetic and natural standards for the other elements were used.

Scanning of zoned chromite grains was done at the Ore Deposits Geology Institute, University of Athens, by electron microprobe Cambridge Microscan 5. Pure metal for Fe, Cr and Mn and synthetic standards for Al and Mg were used.

Chemistry

The chromite cores can be classified as Cr-rich chromites, especially those from the Edessa and Olympus regions, where the ratio of Cr/(Cr+Al) is 0.85 (Fig. 2). The aluminium and magnesium content is low (Table 1). The unusually high manganese content ranges from 0.3 to 0.9 wt.% MnO at Vermion. 2.2 to 5.9 wt.% MnO at Olympus and 1.7 to 9.9 wt.% MnO at Edessa region (Economou, 1979), with very low V and Zn.

Electron microprobe determinations across the zoned chromite show considerable variation. Mn, Cr, Al and Mg decrease as Fe and Ni increase outward from the chromite core to the magnetite rim (Figs. 3, 4 and 5). In the intermediate zone of ferrit-chromit,

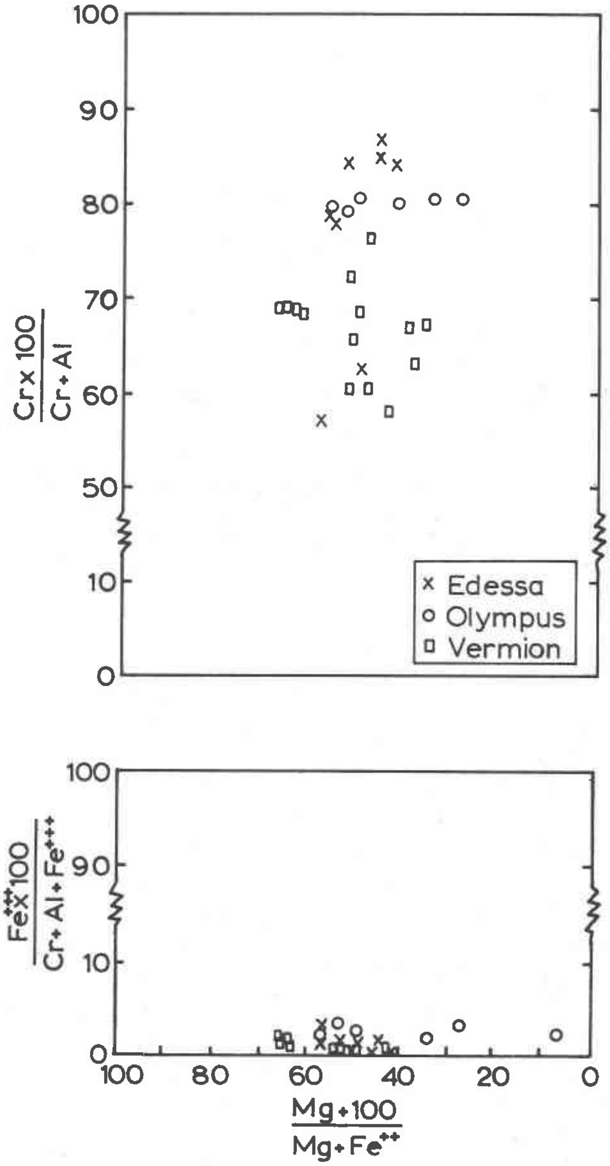

Fig. 2. Variation of Cr/(Cr+Al) and Fe^{3+}/(Cr+Al+Fe^{3+}) ratios against Mg/(Mg+Fe) ratio in chromite cores from various localities. The diagram is based on data of Economou (1979).

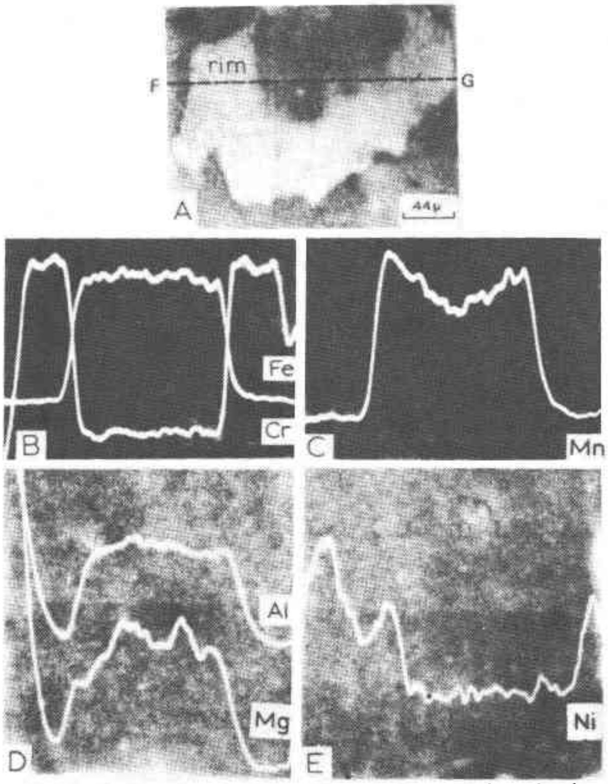

Fig. 3. Back-scattered electron image of zoned chromite from Edessa region. Electron microprobe profiles of Cr, Fe (B), Mn (C), Al, Mg (D), and Ni (E) along the line F–G of the Figure 3A.

as well as in the periphery of chromite core, Mn content attains its greatest values, up to 14.4 wt.% MnO (Table 1).

There is great variability of manganese content in the zoned chromite grains. Chromite cores from various regions or from a given specimen, with similar Cr content, show a large range in the manganese content (Fig. 6). Microprobe profiles across zoned chromite grains indicate that the Mn content in the Mn-rich intermediate zone is proportional to the thickness of the magnetite rim. Zoned grains with small magnetite rims have Mn contents in enrichment zones lower than grains with large magnetite rims. Also chromite grains with an asymmetric magnetite rim show an asymmetric distribution of Mn (Fig. 5). Such a distribution of Mn is common in zoned chromite grains both in massive ore and in chromite grains disseminated within serpentinites and talc schist adjacent to massive ore. It is known that the manganese from the primary chromite grains is not provided by the gangue minerals, as chlorite, garnet and idocrase, have zero or very low Mn (Economou, 1979). It is clear, therefore, that a correlation exists between the Mn content in the enrichment zone and the manganese released from the part of chromite grain already transformed to magnetite.

The above hypothesis is also supported by the

Table 1. Electron microprobe analyses of zoned chromite grains

	1	2	3	4	5	6	7	8	9	10	11
SiO_2	0.00	0.00	0.00	0.00	0.15	0.40	0.00	0.26	0.18	0.29	0.93
Al_2O_3	8.99	9.87	9.33	6.71	7.29	6.15	14.18	6.07	7.46	8.82	0.00
Cr_2O_3	59.46	59.60	59.64	62.43	60.79	61.99	56.36	43.95	38.26	37.04	0.48
Fe_2O_3	1.36	1.85	2.39	1.49	1.87	0.51	0.38	17.08	20.61	29.17	67.34
TiO_2	0.00	0.00	0.00	0.08	0.11	0.03	0.10	0.00	0.00	0.00	0.30
MgO	6.26	9.50	9.29	6.58	6.24	6.07	10.47	1.08	0.70	0.20	0.22
FeO	21.68	13.06	15.56	14.42	15.76	12.76	17.44	26.36	24.99	16.26	28.99
MnO	2.21	5.88	3.66	8.53	7.51	9.88	0.58	4.39	6.29	14.41	0.00
NiO	0.00	0.00	0.00	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.96	99.76	99.89	100.33	99.72	97.85	99.51	99.19	98.49	98.19	99.18
Number of cations on the basis 32 (O)											
Si	—	—	—	—	0.103	0.112	—	0.075	0.075	0.088	0.286
Al	2.993	3.096	2.941	2.166	2.363	2.036	4.343	2.081	2.570	0.923	—
Cr	12.829	12.534	12.579	13.513	13.201	13.762	11.576	10.106	8.842	8.927	0.116
Fe^{3+}	0.279	0.370	0.480	0.307	0.039	0.108	0.074	3.738	4.534	6.691	15.563
Ti	—	—	—	0.017	0.023	0.007	0.020	—	—	—	0.069
Mg	2.542	3.766	3.473	2.685	2.555	2.541	4.054	0.468	0.306	0.092	0.101
Fe^{2+}	4.948	2.906	3.694	3.302	3.620	3.011	3.789	6.413	6.110	4.145	7.445
Mn	0.508	1.327	0.834	1.978	1.746	2.351	0.128	1.082	1.558	3.720	—
Ni	—	—	—	0.017	—	—	—	—	—	—	0.227
Total	24.00	24.00	24.00	23.98	23.65	23.92	23.98	23.96	23.97	23.96	23.80

1-3: Olympus region, 4-6: Edessa region and 7-11: Vermion region. Fe_2O_3 and FeO calculated from total Fe assuming that R_2O_3:RO=1. Analyst: M.Economou.

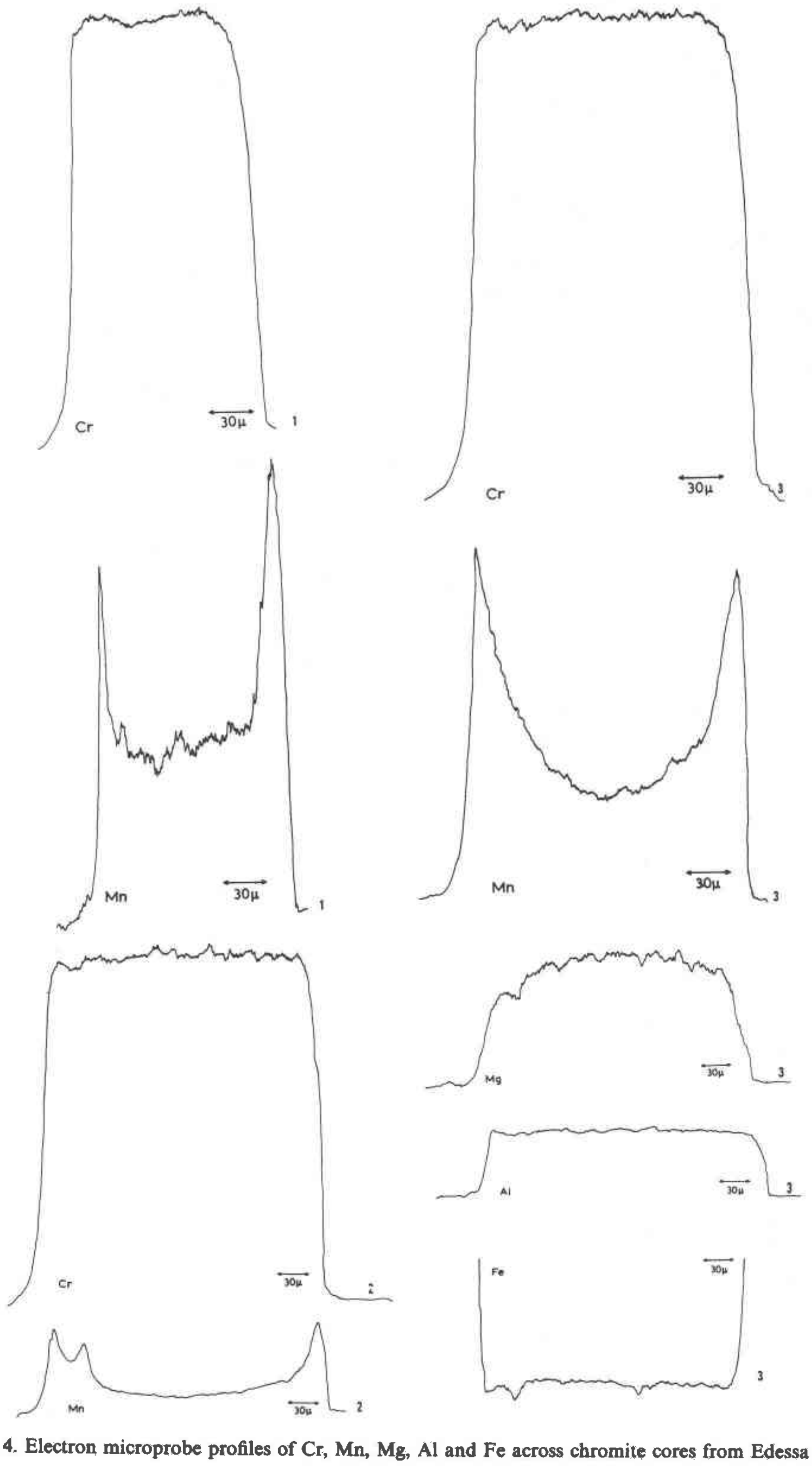

Fig. 4. Electron microprobe profiles of Cr, Mn, Mg, Al and Fe across chromite cores from Edessa region.

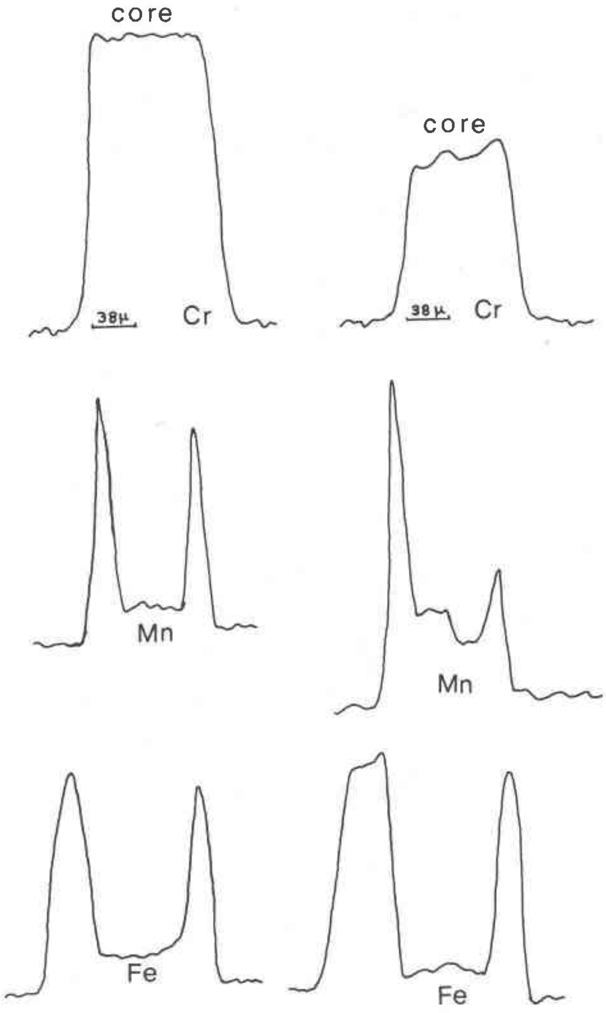

Fig. 5. Electron microprobe profiles of Cr, Mn and Fe across zoned chromites with asymmetric magnetite rim, showing also an asymmetric distribution of Mn in the intermediate zone.

manganese distribution in the zoned chromite grains. A significant number of microprobe analyses and profiles across zoned chromite grains with a more or less symmetrical magnetite rim were made so that the magnetite rim, Mn-rich zone, and the chromite core were each analyzed. The results indicate that the surface area ratio of magnetite rim to that of Mn-rich zone is approximately equal to the ratio of the manganese concentration in the Mn-rich zone to manganese concentration in the chromite core. Figure 7 illustrates a simplified means for estimating this relation. R_1 is the radius of the original chromite grain, R_2 is the radius of the chromite core plus Mn-rich zone, and R_3 is the radius of the chromite core. The surface area of magnetite rim can be expressed as the difference in surface area between original chromite grain (S_1) and chromite core plus Mn-rich zone (s_2), *i.e.*, $S_1 = \pi R_1^2$ and $S_2 = \pi R_2^2$. Thus the surface area of magnetite rim is $S_3 = S_1 - S_2$ and that of Mn-rich zone is $S_4 = \pi R_2^2 - \pi R_3^2$. If the concentration of Mn in the chromite core is C_1 and that in Mn-rich zone is C_2, then the ratio S_3/S_4 is about equal to the ratio C_2/C_1. As an example, in a zoned chromite grain with $R_1 = 50$ μ, $R_2 = 33$ μ and $R_3 = 17$ μ the measured values of magnanese were 3.0 wt.% Mn in the chromite core and 5.8 wt.% Mn in the Mn-rich zone, whereas in magnetite rim it is negligible. In this case the ratio $S_3/S_4 = 1.8$ and $C_2/C_1 = 1.9$.

Discussion

It is clear that the described Mn-rich phases (Table 1, Figs. 3, 4 and 5) have compositional variation ranges previously unknown in chromite compositions (Stevens, 1944; Hiessleitner, 1951, 1952; Irvine, 1967; Evans and Frost, 1975; Greenbaum, 1977; Groves *et al.*, 1977; Sinton, 1977; Dick, 1977).

The chromites of the iron meteorites show a unique chemistry as they contain appreciable amounts of MnO and ZnO. These chromites coexist with almandite and sphalerite, and they establish both the chalcophile and lithophile behavior of these

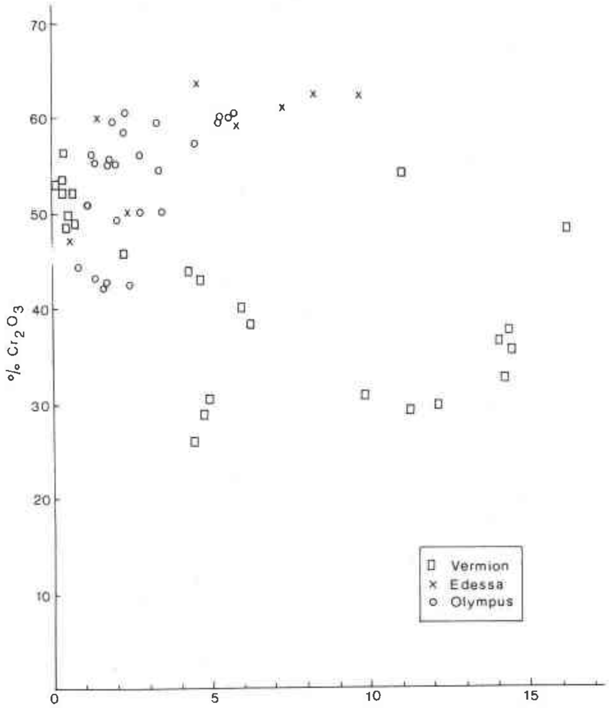

Fig. 6. Relationship between MnO and Cr_2O_3, in weight percent, of analyzed zoned chromites. The diagram is based on data from Economou (1979).

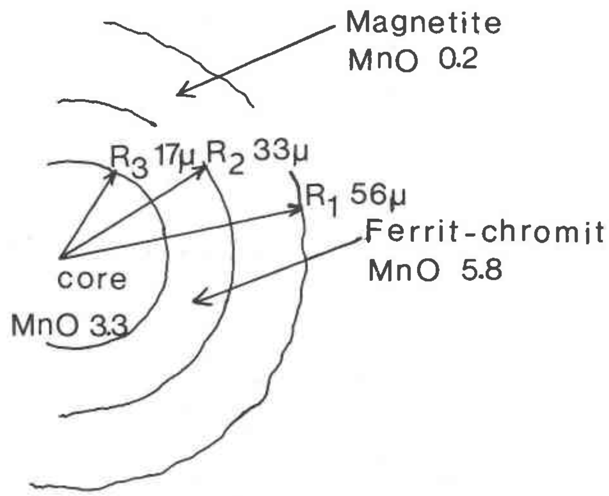

Fig. 7. Sketch of zoned chromite grain showing the relationship between surface area and Mn content, in weight percent, of Mn-rich zone and magnetite rim.

two elements in iron meteorites (Goresy and Kullerud, 1969). Terrestrial spinels with high Mn content are known from the La Perouse layered gabbro, Alaska. They are poor in Al_2O_3, MgO and TiO_2, but the concentration of MnO and V_2O_3 are unusually high. Czamanske *et al.* (1976) suggest that this chromite has crystallized at low oxygen fugacity and at temperatures above 900°C. Also manganochromite is known, at the Nairne sedimentary pyrite deposit, South Australia, but it has a very high V content (Graham, 1978).

Direct evidence regarding the nature of the original magma from which the chromites of northern Greece crystallized is not available and the relatively high manganese content is not easily explained at the present time. However, because of its high manganese content the intermediate zone may be indicative of the progressive metasomatism of chromite to ferrit-chromit and finally to magnetite.

Concerning the conditions of genesis of zoned chromite, the opinions of authors vary (Golging and Bayliss, 1968; Beeson and Jackson, 1969; Ulmer, 1974; Bliss and MacLeen, 1975; Groves *et al.*, 1977, Economou, 1979).

The heterogeneous Mn content of chromite cores with a similar Cr content (Fig. 6) and the asymmetry of the Mn picks in electron microprobe profiles across zoned chromite grains, depending on the degree of development of the magnetite rim (Fig. 5) provide supporting evidence for a secondary enrichment in Mn in the zoned grains and its derivation from the Mn contained in the primary chromite. Therefore, the high Mn content in the ferrit-chromit zone, in the periphery of the chromite core, and occasionally in the core itself, may be interpreted as the result of the substitution of Mn for Mg and in part for Fe^{2+}. The Mn ions are derived from the other parts of the chromite grains which have transformed to magnetite and/or from the adjacent small grains of original chromite which transformed completely to magnetite. This aspect is also supported by the symmetrical manganese peaks for the zoned chromite grains with symmetrical magnetite rims. As mentioned above, the ratio of the surface area of magnetite rim to that of Mn-rich zone is approximately equal to the ratio of the Mn concentration of the Mn-rich zone to that of chromite core. Thus, the manganese variation may be indicative of the progressive metasomatism of chromite.

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