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Zincian, manganiferous chrome spinel from the Swat valley ophiolite, NW Pakistan

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ABSTRACT: *Metamorphosed basic volcanic rocks of the Swat valley ophiolite locally contain trace to accessory amounts of disseminated chrome spinel. The grains of chrome spinel are invariably altered along margins and fractures. They, therefore, consist of low-reflectance (grey) cores/ patches that are bordered and traversed by highly reflectant (bright) zones. Compositionally, the cores are high-Cr, almost Mg-free chromites, containing unusually high amounts of Zn and Mn, and may thus be described as a solid solution of three end-member spinel compositions, i.e. chromite, gahnite and galaxite. The bright zones of alteration lack any notable amount of Zn or Mn and range from Cr-mangnetite to magnetite. Compositional and textural relationships suggest that the markedly zincian and manganoan character of the spinel grains is the result of a hydrothermal activity that took place before the magnetite-forming alteration process. The Zn-, Mn-bearing hydrothermal fluids either reacted with the parental lava prior to or during its solidification or, alternatively, invaded the host rocks after their formation leading to the addition of Zn and Mn to, and concomitant removal of Mg from, the already crsytallized magmatic chromite through dissolution-recrystallization.*

INTRODUCTION

Chrome spinel rich in Zn is considered unusual enough to be reported in the literature (Wylie et al., 1987). A ZnO content of >0.5 wt % in chrome spinel is considered significant (Groves et al., 1983). The natural occurrence of zincian spinel is relatively rare. This is believed to be due to geochemical rather than crsytallographic control (Moore, 1977). However, spinels with unusually high amounts of Zn ± Mn ± V are reported from quite a few localities. These include Helgeland, Norway (Donath, 1931; Moore, 1977), Piedmont upland, Maryland, Pennsylvania (Pearre and Heyl, 1960), Outokumpu, Finland (Thayer et al., 1964; Weiser, 1967), Western Australia (Groves et al., 1977), Mashaba, Zimbabwe (Bevan and Mallinson, 1980), Plan d'Albard, Italy (Wagner and Velde, 1985), Sykesville district of Maryland (Wylie et al., 1987), Kuså, Bergslagen, Sweden (Zakrzewski, 1989), Atik Lake area, Manitoba (Bernier, 1990), and Salsigne, France (Béziat and Monchoux, 1991). This study reports and describes the occurrence, and textural and chemical characteristics of disseminated zincian, maganoan chrome spinel grains (containing up to 4.4 wt % ZnO and 3.17 wt % MnO) from the metamorphosed basic volcanic rocks of the Swat valley ophiolite, NW Pakistan.

GENERAL GEOLOGY AND HOST ROCK CHARACTERISTICS

Rocks of ophiolitic affinity occur in the Swat valley, NW Pakistan. They constitute what is termed as the Mingora ophiolitic melange - one of the three types of melanges distinguished in the area (Kazmi et al., 1984). In addition to other typical lithologies, the ophiolitic melange contains different types of volcanic rocks. The Spini Obo section of the ophiolite can be termed a type locality for the occurrence of such rocks (Fig. 1).

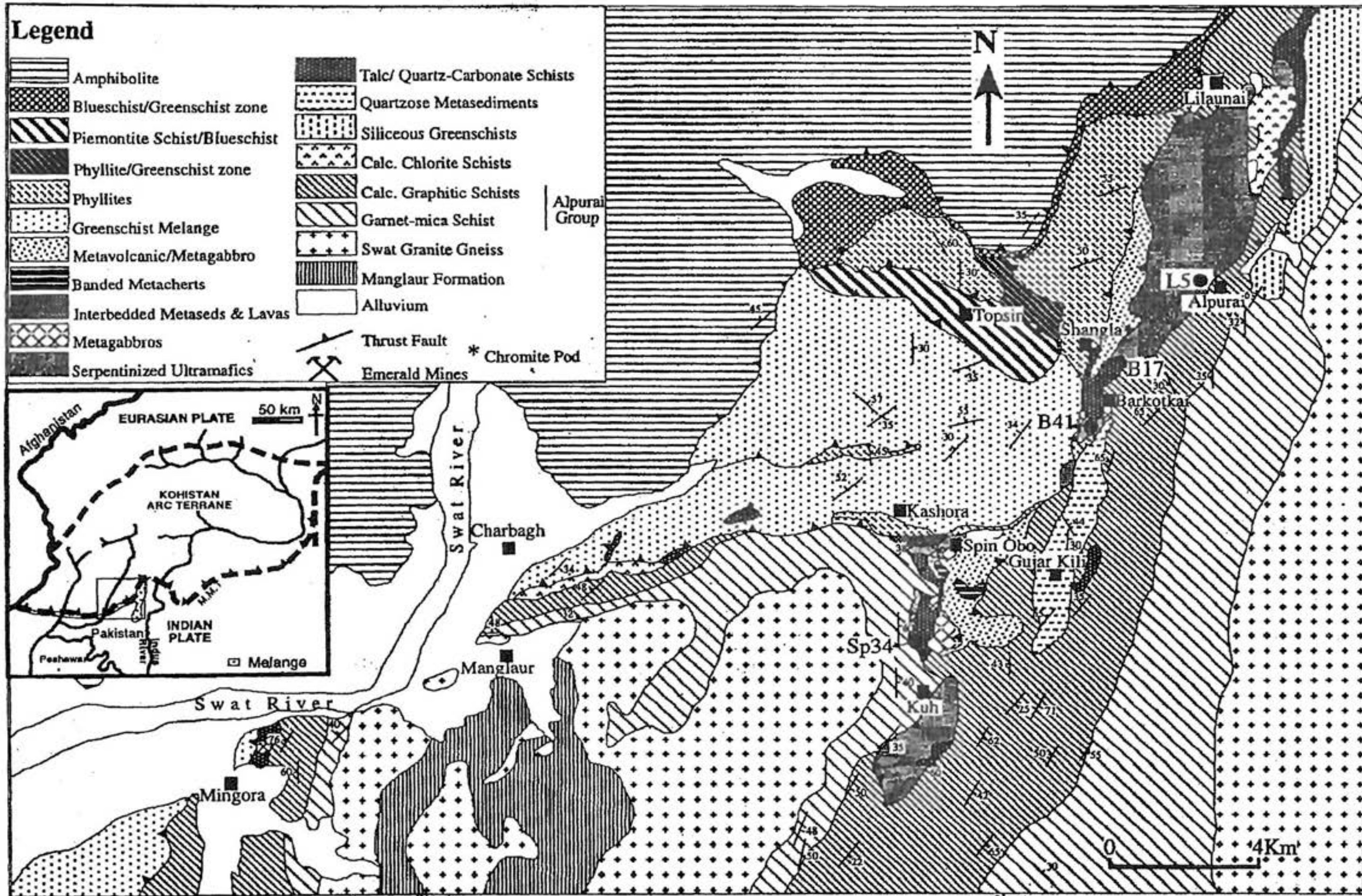

Fig. 1. Geological map of the Mingora-Lilaunai area Swat, NW Pakistan (after Hussain et al., 1982; Kazmi et al., 1984). The inset map shows general location of the study area.

Like other components of the Swat valley ophiolite, basic lavas from the Spini Obo area are extensively metamorphosed under upper greenschist to lower amphibloite facies conditions (Arif and Moon, 1996). However, their formation as a result of submarine volcanic eruption is still evident from the locally well preserved, though now invariably deformed, relict pillow structures.

The pillowed basaltic rocks from the Spini Obo area consist of sodic plagioclase, calcic amphibole, epidote, chlorite, quartz, calcite, magnetite and chrome spinel. The plagioclase and epidote locally occur as porphyroblasts. The epidote grains show marginal alteration to chlorite. The chlorite outer rim is itself surrounded by a zone of a dirty stuff that contains granules of opaque(s). The grains of chrome spinel also display alteration along fractures and margins (Fig. 2).

CHEMISTRY OF CHROME SPINEL

The optically inhomogeneous grains of chrome spinel were analyzed through Jeol Superprobe model JXA-8600 with an on-line computer for ZAF corrections. Quantitative analyses were conducted using wavelength dispersive system and natural and synthetic standards under the following operating conditions: 15 Kv accelerating voltage; 30 x 10^{-9} A probe current; 20 (2 x 10) seconds peak, 10 (2 x 5) seconds negative background and 10 (2 x 5) seconds positive background counting times. The accuracy of the ZAF correction is generally better than 2 %.

The grey (unaltered) cores mainly consist of (wt %) Cr_2O_3 (53.54-54.21), Al_2O_3 (7.09-7.20), FeO (25.55-26.73), Fe_2O_3 (4.49-5.40), ZnO (2.75-4.41), and MnO (2.98-3.17). Besides, they also contain small but significant

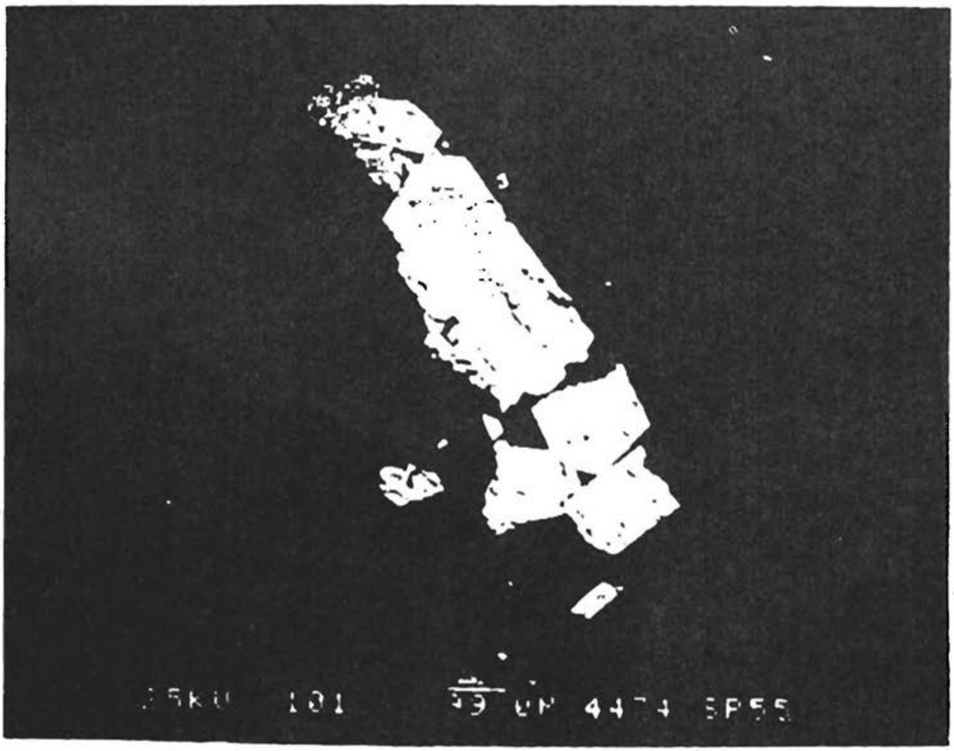

Fig. 2. A back-scattered SEM image of a chrome spinel grain consisting of zones of magnetite/ Cr-magnetite (bright) and unaltered (relict) patches of Zn-, Mn-bearing, high-Cr chromite (grey).

amounts of MgO (0.17-0.51) and V_2O_3 (0.18-0.28), as well as traces of TiO_2 (0.10-0.15) and NiO (0.03-0.12). Accordingly, they are characterized by invariably high Cr #s [100 x Cr/ (Cr+Al) = 83.4-83.7], relatively low Fe^{3+} #s [100 x Fe^{3+}/ (Cr+Al+Fe^{3+}) = 6.2-7.4], and very low Mg #s [100 x Mg/ (Mg+Fe^{2+}) = 1.2-3.2] (Table 1).

Mn and Zn show negative correlation with both Mg and Fe^{2+}. The negative correlation of Mn with both Mg and Fe^{2+} is relatively less significant. On the other hand, the negative correlation of Zn with both Fe^{2+} and Mg is highly significant (Fig. 3). The very high value of correlation coefficient for a plot including the sum of Mn and Zn versus Mg plus Fe^{2+} strongly suggests that the former pair substitute for the latter. The analyses contain almost equal amounts of Mn and Zn (Fig. 4).

A detailed comparison with unaltered cores suggests that the alteration zones are strongly impoverished in Cr, Al, Zn, Mn, Mg, Ti and V, but markedly enriched in both Fe^{3+} and Fe^{2+}. In fact, their only notable component, besides Fe, is Cr_2O_3 (0.41 to 2.36 wt %) (Table 1). Because of extensive substitution of Fe for other components, e.g. Cr (Fig. 5), the zones of alteration range from chrome magnetite to magnetite in composition.

DISCUSSION AND CONCLUSIONS

The unaltered, grey cores of the studied chrome spinel grains are high-Cr chromites containing anomalously high amounts of Zn and Mn. They thus appear to represent a solid solution among three end-member spinel compositions: Mg-, Al-, Fe^{3+}-bearing chromite ($FeCr_2O_4$), gahnite ($ZnAl_2O_4$) and galaxite ($MnAl_2O_4$) (Fig. 4).

The occurrence of magnetite/ Cr-magnetite along fractures and boundaries of chrome spinel grains suggests its formation during the alteration and/ or metamorphism of the host rock. A survey of the relevant literature also supports such a mechanism for the development of this phase. As mentioned earlier, whereas the relict chromite cores contain abnormally high amounts of Zn and Mn, the alteration product (magnetite) is virtually free of these components. This observation clearly indicates that the addition of these two elements, if not a primary (purely magmatic) phenomenon, is at least genetically unrelated to the process of alteration that leads to the development of Cr-magnetite zones. In other words, the formation of, and/ or incorporation of Zn and Mn into, the chrome spinel cores clearly predates the process of formation of Cr-magnetite. The following two alternative mechanisms are proposed for the presence of unusually high amounts of Zn and Mn in the otherwise high-Cr chromite from the pillowed metabasaltic rocks of the Swat valley ophiolite:

1. Prior to or during its solidification, lava parental to the investigated rocks acquired high values of Zn and Mn through a reaction with Zn, Mn-bearing hydrothermal fluids probably related to submarine or volcanogenic exhalative activity at the ocean floor. These elements entered into the structure of the crystallizing chrome spinel grains taking the place of the more commonly occurring divalent cations, i.e. Mg (and Fe^{2+}), of spinel.
2. The anomalously high Zn and Mn contents in the studied chrome spinel grains reflect an origin involving dissolution-recrystallization from 'normal' magmatic Cr-bearing spinels. The abnormally low Mg and its inverse relationship with Zn and Mn contents of the investigated chromite indicate that Mg was removed as Zn and Mn were added.

TABLE 1. MICROPROBE ANALYSES OF CHROME SPINEL

Anal.	Core-1	Margin-1	Core-2	Margin-2	Core-3	Margin-3	Core-4	Margin-4	Core-5	Margin-5	Core-5	Margin-5
TiO_2	0.14	0.02	0.12	0.01	0.15	0.02	0.10	0.01	0.11	0.00	0.11	0.01
Al_2O_3	7.09	0.02	7.15	0.00	7.16	0.03	7.20	0.02	7.20	0.02	7.11	0.18
Cr_2O_3	54.13	2.36	53.54	0.42	53.67	2.08	54.21	2.20	54.11	0.41	53.55	1.22
V_2O_3	0.24	0.13	0.18	0.16	0.24	0.16	0.20	0.16	0.27	0.21	0.28	0.07
Fe_2O_3	4.49	66.21	5.03	67.7	5.40	65.92	4.65	66.49	4.90	67.56	5.24	65.99
FeO	26.13	30.84	25.82	30.62	26.10	30.68	26.47	30.91	26.73	30.59	25.55	30.43
MnO	2.98	0.09	3.09	0.05	3.11	0.03	3.16	0.05	3.05	0.03	3.17	0.08
MgO	0.20	0.00	0.21	0.01	0.22	0.01	0.22	0.01	0.51	0.02	0.17	0.12
CaO	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.01	0.00	0.01	0.02	0.00
NiO	0.12	0.04	0.09	0.05	0.03	0.02	0.07	0.02	0.03	0.02	0.03	0.02
ZnO	3.78	0.04	3.95	0.02	4.02	0.03	3.31	0.06	2.75	0.02	4.41	0.01
Total	99.31	99.76	99.19	99.04	100.11	98.98	99.6	99.94	99.66	98.89	99.64	98.13

Cations per four oxygens

Ti	0.004	0.001	0.003	0.000	0.004	0.001	0.003	0.000	0.003	0.000	0.003	0.000
Al	0.304	0.001	0.307	0.00	0.305	0.001	0.308	0.001	0.307	0.001	0.304	0.008
Cr	1.558	0.072	1.543	0.013	1.533	0.064	1.554	0.067	1.546	0.013	1.538	0.038
V	0.007	0.004	0.005	0.005	0.007	0.005	0.006	0.005	0.008	0.007	0.008	0.002
Fe^{3+}	0.123	1.922	0.138	1.981	0.147	1.929	0.127	1.927	0.133	1.98	0.143	1.941
Fe^{2+}	0.796	0.995	0.787	0.996	0.789	0.998	0.803	0.995	0.808	0.996	0.776	0.995
Mn	0.092	0.003	0.095	0.002	0.095	0.001	0.097	0.002	0.093	0.001	0.098	0.003
Mg	0.011	0.000	0.011	0.001	0.012	0.001	0.012	0.001	0.027	0.001	0.009	0.007
Ca	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
Ni	0.004	0.001	0.003	0.002	0.001	0.001	0.002	0.001	0.001	0.001	-0.001	0.001
Zn	0.102	0.001	0.106	0.001	0.107	0.001	0.089	0.002	0.073	0.001	0.118	0.000
Cr #[1]	83.67	98.63	83.41	100.00	83.41	98.46	83.46	98.53	83.43	92.86	83.50	82.61
Mg #[2]	1.36	0.00	1.38	0.10	1.50	0.10	1.47	0.10	3.23	0.10	1.15	0.70
Fe^{3+} #[3]	6.20	96.34	6.94	99.35	7.41	96.74	6.39	96.59	6.70	99.30	7.20	97.68

1 100 x Cr/ (Cr+Al)
2 100 x Mg/ ($Mg+Fe^{2+}$)
3 100 x Fe^{3+}/ ($Cr+Al+Fe^{3+}$)

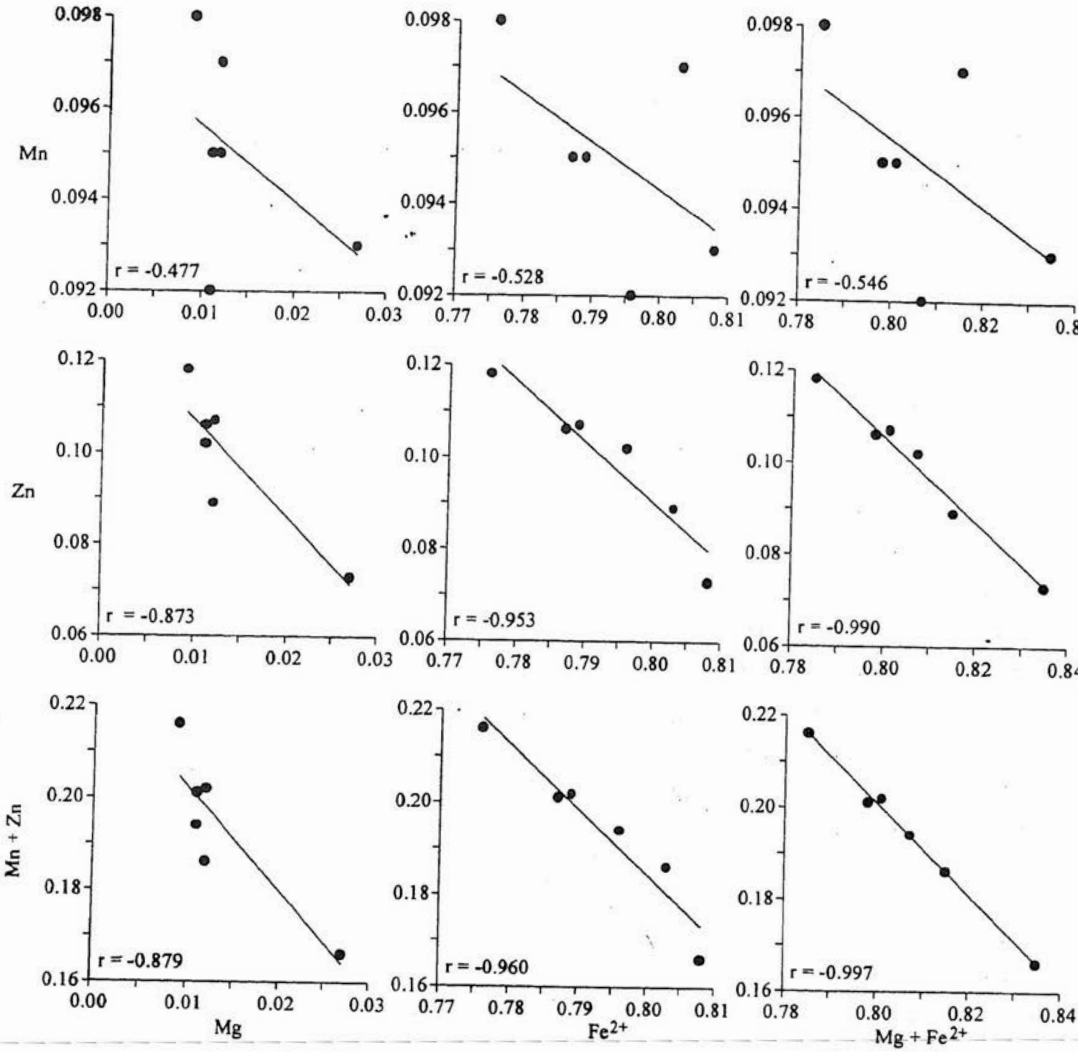

Fig. 3. Relationship of Zn and Mn with Mg and Fe^{2+} in the investigated unaltered chrome spinel.

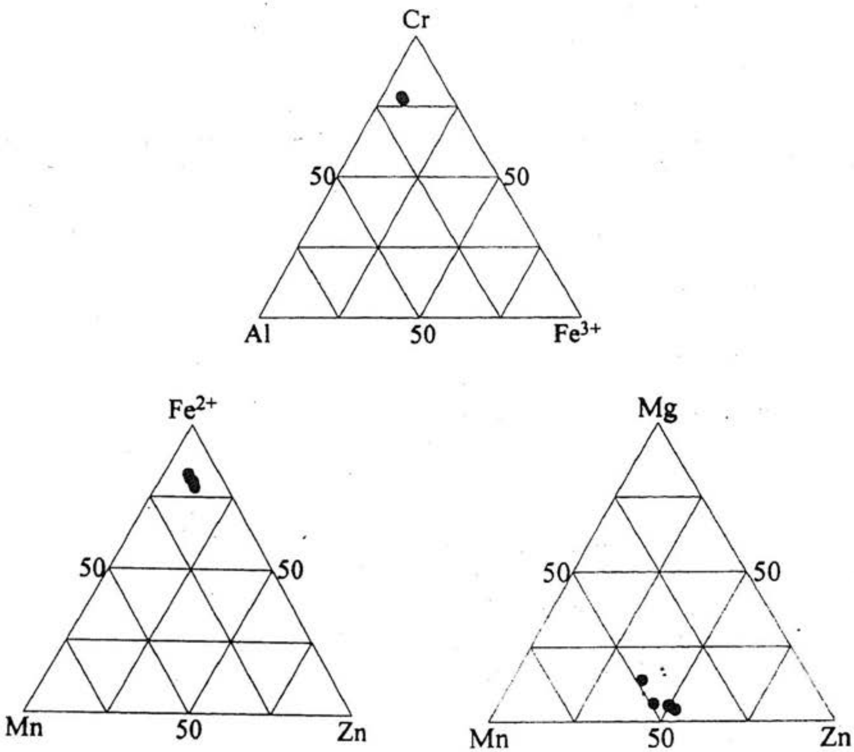

Fig. 4. Compositional characteristics of the investigated unaltered chrome spinel.

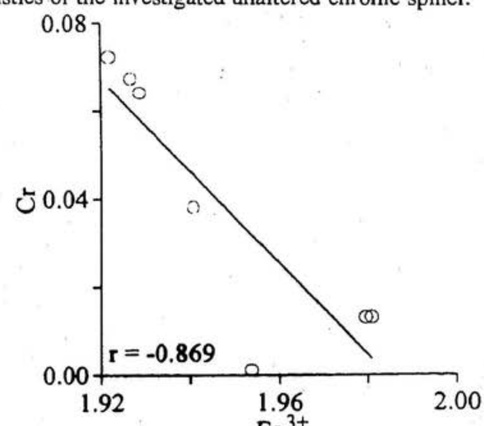

Fig. 5. Cr-Fe3+ relationship in the magnetite/ Cr-magnetite bright zones around the grey, unaltered Zn-, Mn-bearing, high-Cr chromite.

After its formation through one of the two possibilites, mentioned above, the Zn-, Mn-bearing chromite underwent a further process of modification leading to its transformation to Cr-magnetite. This most probably took place through yet another episode of alteration and/ or regional metamorphism of the host rock. Assuming the second mechanism for the formation of Zn-, Mn-bearing chromite, the present compositional and textural characteristics of the Cr-spinel grains appear to be the result of two separate events of alteration, as summarized below:

1. High-Cr, Mg-chromite (magmatic) + Zn+Mn (hydrothermal) → Mg-poor/ free, Zn-, Mn-bearing, high-Cr chromite
2. Zn-, Mn-bearing, high-Cr chromite → Cr-magnetite/ magnetite

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