GEOL. CROAT.	47/1	83 - 102	7 Figs.	9 Tabs.	6 Pls.	ZAGREB 1994

A Zincian Chrome-Spinel from the Cr-Ba-Fe-Cu-Zn Deposit near Busovača (Bosnia and Herzegovina)

Ivan **JURKOVIĆ**[1] and Milko **JAKŠIĆ**[2]

Key words: Zincian chrome-spinel, Composition, Genesis, Alteration, Busovača, Bosnia

Ključne riječi: cinkov krom-spinel, sastav, postanak, alteracije, Busovača, Bosna

Abstract

The metamorphic complex of the Busovača area is mostly composed of Upper Silurian-Lower Devonian metapelites, metapsammites and metarhyolites formed under low grade metamorphism at 350° to 450°C and 3 to 5 kbars. The ore minerals of the Busovača deposit are: magnetite (with relics of zincian chrome-spinel), rimmed by ferrichromite, and pyrite, chalcopyrite, enargite, bornite and siegenite. The gangue minerals are: siderite, quartz, albite, hyalophane, muscovite, chromian-chlorite and manganoan ankerite. Proton microprobe analyses (PIXE) were made of samples A (core Ac of the slightly altered chrome-spinel), B (strongly altered chrome-spinel with Bc-core, Bfc-ferrichromite zones, Br-magnetite rim) and C (cryptically zoned magnetite with Cc-core and Cr-magnetite rim). The results are recalculated in formulae, and presented on separate diagrams.

The optical investigations, microprobe analyses, beam-scan photographs, diffusion rates of Mg, Al, Zn, Cr, and Mn, and diagrams, allow the following conclusions to be made: (1) magmatic origin of the primary chrome-spinel, (2) the emplacement of the Zn was prior to the alteration under very low f_{O_2}, most probably synchronous with the sulphide mineralization; (3) the alteration process took place in two phases: (a) the early stage volume-for-volume replacement and formation of the ferrichromite and magnetite zones, (b) the late stage characterized by decolourization and/or resorption, and/or dissolution of the core (patches, specks, "atoll structure"); (4) released Al, Cr, Mn, and Zn have been taken up by silicate, carbonate and oxide minerals forming chromian-chlorite, manganoan ankerite or contaminated siderite and pyrite; (5) the diffusion rates among Al, Zn, Cr, and Mn during different stages of the alteration have the following sequence: Al → Zn → Cr → Mn; (6) the optically unzoned magnetite crystals or aggregates originated in chrome-spinel; (7) the mineral assemblage of the Busovača deposit co-exists with the surrounding metamorphic complex belonging to the greenschist facies.

Sažetak

Metamorfni kompleks Busovače koji je izgrađen pretežito od metapelita, metapsamita i metariolita silursko-devonske starosti formiran je u uvjetima niskog metamorfizma pri 350° do 450°C i 3-5 kbara. Glavni rudni mineral ležišta Busovača je magnetit s ostacima cinkovog krom-spinela obrubljenog feritkromitom, a od ostalih minerala važniji su pirit i halkopirit među rudnim te siderit, kvarc, albit, hijalofan, Mn-ankerit, Cr-klorit među mineralima jalovine. Metodom PIXE analizirana je jezgra zrna krom-spinela u ranoj fazi alteracije (Ac), zatim jezgra (Bc), feritkromitne zone (Bfc) i magnetitni rub (Br) alteracijom jako zahvaćenog kristala B te magnetitni porfiroblast, optički homogen, ali kemijski zonalan (Cc i Cr). Na temelju tih rezultata izračunate su formule, konstruirani dijagrami, te izvedeni slijedeći zaključci: (1) magmatsko porijeklo krom-spinela; (2) zamjena Mg sa Zn u vrijeme sulfidizacije; (3) odvijanje procesa alteracije u dvije faze (a) ranoj, po principu "volume for volume" s očuvanjem kristalnih oblika te stvaranje feritkromita i magnetita, (b) kasnoj s dekolorizacijom, korozijom i resorpcijom jezgre; (4) ugrađivanje Al, Cr, Mn, Zn difundiranih pri alteraciji u Cr-klorit, Mn-ankerit, siderit, pirit, (5) smanjenje brzine difuzije u sekvenci: Al → Zn → Cr → Mn, (6) nastanak optički homogenih magnetita iz krom-spinela; (7) koegzistencija parageneze ležišta Busovača s paragenezama okolnih metamorfnih stijena koje pripadaju faciji "zelenih škriljavaca".

1. GEOLOGY, TECTONIC SETTING AND PARAGENESIS OF THE BUSOVAČA DEPOSIT

The Busovača area is situated in the northeastern part of the Mid-Bosnian Ore Mountains which are included in the Dinaric system (Fig. 1).

The metamorphic complex of this area is built up mostly of chlorite-muscovite-quartz schists, and quartz-sericite schists, locally quartz-graphite schists and restricted lenses of subgraywacke metasediments. Occurrences of amphibole-tremolite or tremolite-sericite schists (orthometamorphites) are very rare (Fig. 2). The metaclastic series is interpreted as Silurian, and in the overlying rocks as Lower and Middle Devonian (ŽIVANOVIĆ et al., 1967; SOFILJ et al., 1980). MAJER et al. (1991) concluded that the metamorphic strata in the area of Busovača were mostly formed by low grade metamorphism at 350-450°C and intermediate pressure of 3 - 5 kbars, locally 5 kbars. The mineralogy consists of quartz, white mica, phengitic muscovite, albite, ripidolite-chlorite, chloritoids (8-26 mole % of Mg component), actinolite, epidote and subordinate stilpnomelane, pumpellyite, pyrophyllite and barroisitic amphibole.

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[1] Faculty of Mining and Geology, University of Zagreb, Pierottijeva 6, 41000 Zagreb, Croatia

[2] Institute "Ruđer Bošković", Bijenička c. 54, 41000 Zagreb, Croatia

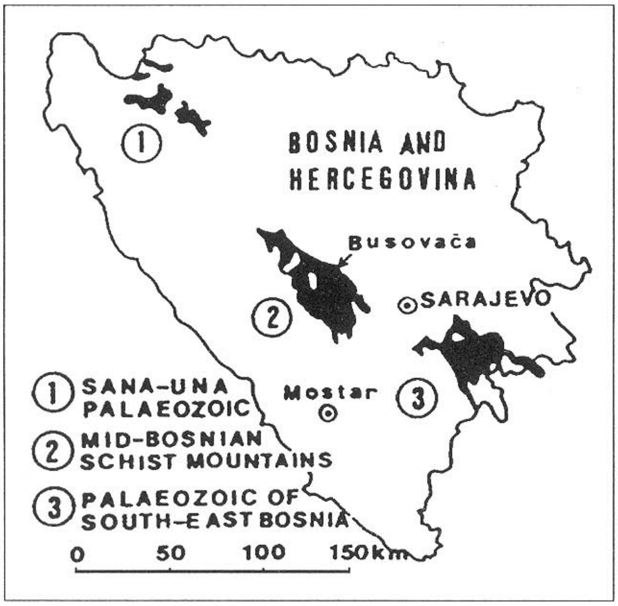

Fig. 1. Palaeozoic areas (1, 2 and 3) in Bosnia and Herzegovina. Location of the Busovača deposit in the Mid-Bosnian Schist Mountains.

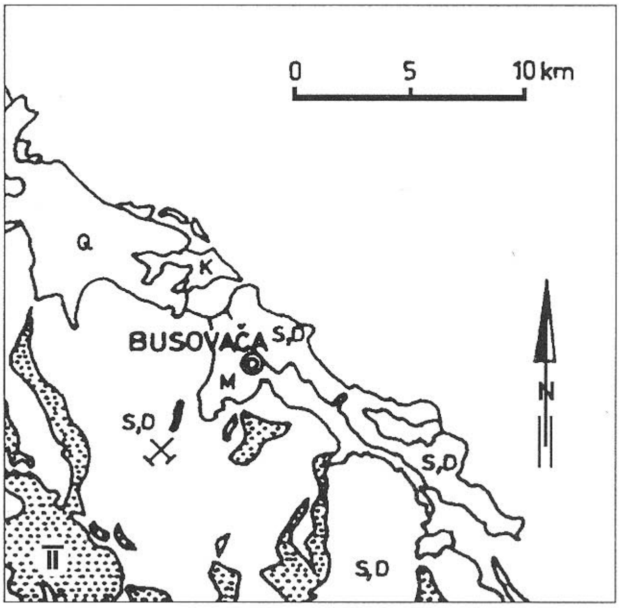

Fig. 2. Geological sketch-map of the Busovača area. Legend: S, D Upper Silurian-Lower Devonian: Π metarhyolites: K Cretaceous; M Miocene; Q Quaternary; / metabasite: ⚒ Busovača deposit.

KATZER (1910) first reported the presence of magnetite and pyrite north of the village Gola Glavica, on the southern bank of the Zagrlski potok and at Peska. In the valley of Zagrlski potok DIVLJAN & SIMIĆ (1954) discovered and described some vertical quartz-hyalophane veins cutting the schists containing calcite, siderite, magnetite and chalcopyrite. JURKOVIĆ (1956) and SIMIĆ (1956) investigated this occurrence independently in detail and defined it as a metamorphosed (Jurković) and high hydrothermal ore (Simić). SIMIĆ (1956) first reported chromian spinel cores within some magnetite grains, as well as ribbons (bands) of chromian chlorite indicated by qualitative spectral analysis. BARIĆ (1957) cites in his paper the Cr_2O_3 contents (0.27 and 0.30 wt %) from the average magnetite sample (prepared from the whole perpendicular profile of the deposit and analysed by Jurković).

The studied zincian spinel is included in the paragenesis of the magnetite-pyrite-chalcopyrite deposit at Zagrlski potok (brook) which occurs 5 km southwest of the town of Busovača (JURKOVIĆ et al., 1992). The mineralization is adjacent to a larger outcrop of a metabasite consisting of green amphibole, albite, pyrite, leucoxene, ilmenite, haematite, sphene, apatite, zircon, and tourmaline, wich appears to be conformable with the surrounding schists. According to TRUBELJA & SIJARIĆ (1970), a narrow zone of alternating dark coloured biotite-chlorite-ankerite schists and light coloured albite-chlorite schists up to 1 m thick separates the metabasite from the metapelites.

The banded ore body represents a rhythmic sequence consisting of a set of parallel or subparallel bands, 0.5-5 cm thick, which differ in colour, texture, structure, and mineral composition. Dark coloured bands, made up of opaque minerals alternate with the light coloured ones of gangue minerals. The individual beds thicken and thin, and their middle parts are characterized by microfolding, microflexures and pressure-shadows (Plate I).

JURKOVIĆ et al. (1992) listed the following minerals in order of decreasing abundance: siderite, quartz, albite, chrome-magnetite, pyrite, manganoan ankerite, hyalophane, zincian chrome-spinel rimmed by chrome-magnetite ± intermediate ferrichromite zone, chalcopyrite, muscovite, chromian chlorite, biotite, enargite, siegenite, millerite, bornite, covellite, idaite, martite, zircon, tourmaline, apatite, ilmenite, leucoxene, silver and gold.

Magnetite is the major opaque mineral. It forms either euhedral crystals or crystal aggregates or myrmekitic intergrowths with gangue minerals. Its grain size in individual layers varies from $\leq$ 3-5 μm, to 1-3 mm porphyroblasts and xenoblasts. Partial quantitative analysis of the sample containing a concentrate of the magnetite grains, comparatively rich in relict chromian-spinel cores, taken from the lower and middle parts of the profile, contains 1.42 wt % Cr_2O_3 indicating an average of 3 wt % of relict chromite within magnetite. The proportion of the narrow ferrichromite zones is almost negligible. Therefore, no other spinel phase was found in altered chromite by X-ray examination. The same results were reported by PETERS & KRAMERS (1974) for zoned chromites from Oman. Most of the magnetite porphyroblasts or fine-grained magnetite aggregates, especially characteristic for the upper part of the profile, are not optically zoned. One larger magnetite crystal showed a cryptical zoning, but without any reflectivity differences (Plate VI). They display specific optical properties respective to a standard magnetite mineral.

The stringers and streaks (1 to 5 mm thick) consisting mainly of magnetite grains in the lower and middle parts of the ore profile have a significant number of optical zoned chromites, visible in polished sections due to reflectivity differences. Optically zoned, well developed chromite grains consist of a dark grey chrome-spinel core surrounded by one or two rims of ferrichromite of higher reflectivity, grading outward to magnetite of high reflectivity. In many optically zoned chromite grains one or both ferrichromite zones or the dark core are lacking (Plates II and III). All four zones are not equally well developed in all samples. The two ferrichromite zones are not present in most of the magnetite grains. The cores and the intermediate zones are not present in the larger disseminated magnetite grains. The relict cores vary from less than 1-3 μm in diameter in the disseminated small grains up to over 100 μm in the larger grains. The width of the ferrichromite zones varies from 1-3 - 10-15 μm. Contacts between the optical zones are usually sharp, but occasionally are not clearly defined and vague. The polishing hardness of the core is greater than that of the ferrichromite or the magnetite rim.

The reflectivity of chrome-spinel is much lower than the outer magnetite zone, particularly in cedar oil. The reflectivity depends on the degree of metamorphism, and therefore its value varies from one grain to another. Some chrome-spinel cores exhibit brownish or red-brownish internal reflections, particularly in cedar oil. The reflectivity of ferrichromite is lighter than that of chrome-spinel, but distinctly darker than that of magnetite. Between the two ferrichromite zones, the inner zone is slightly darker than the outer one. In thin section, the core is slightly transparent.

The shapes of the cores during the early stage of alteration are always euhedral with very different cross-sections that suggest the magmatic origin and excludes a detrital origin of the chrome-spinel (Plate II, Figs. 1, 2, 3 and 4). In this stage of alteration the narrow zones of the ferrichromites have identical or very similar shapes indicating an epitaxial ferrichromite growth, as well as a close genetic mutual relationship. The identical crystal shapes of the chrome-spinel core and outer magnetite rim (which is characterized by the ragged and lobed borders of the grains), are rarely found.

Late stage alteration is characterized by (1) the decolourization of the chrome-spinel cores with a reflectivity increasingly similar to that of ferrichromite (Plate II, Fig. 4; Plate III, Figs. 1 and 2). In some thin sections the decolourized areas are in the form of irregular patches; (2) the irregular penetration of the ferritchromite in the chrome-spinel core (atoll structure) (Plate II, Fig. 6; Plate III, Figs. 1, 2 and 3), and (3) small patches and minute specks as relics of alteration in magnetite (Plate III, Figs. 2, 3, 4 and 5). BLISS & MacLEAN (1975) and MICHAILIDIS (1990) recorded the similar phenomena.

In a final phase chrome-spinel alteration results in optically unzoned chromium-bearing magnetite, locally cryptically zoned (Plate III, Fig. 6).

2. PROTON MICROPROBE DATA

Analyses were performed using the SPM-scanning proton microprobe (WATT & GRIME, 1987). This microbeam instrument at the "Rudjer Bošković" Institute Zagreb, is positioned at one of four beam lines of the EN Tandem Van de Graaff accelerator. The foccusing system is the magnetic quadrupole doublet. The sample is mounted on the sample holder in a vacuum chamber and can be positioned accurately using an XYZ translator. A large solid angle Si (Li) semiconductor detector is used for detecting X-rays. For all measurements, a 3 MeV proton beam with 10 pA current, was used. Typical beam spatial resolution was 2 μm. Multielement standard reference materials were used for testing the PIXE quantitative analysis routine (JAKŠIĆ et al., 1992). By scanning the beam over the sample, accumulated X-ray intensity maps represent the element distribution (Cr, Fe, Zn, Mn, Al and Mg) at the sample surface (beam-scan photographs).

The microprobe analyses (PIXE) were carried out on samples A, B and C. The results of the proton microprobe analyses are presented in the Tables 1, 2 and 3. Formulae are presented in Table 4, the spinel components in Table 5, and the different mutual cation ratios in Table 6. Tables 7 and 8 show the changes in chemical composition of the zincian chrome-spinel during the early (sample A), medium (sample B) and late stages of the alteration process (sample C).

2.1. MICROPROBE ANALYSIS OF THE PRIMARY CHROMITE CORE

Sample A - a chrome-spinel grain was analysed with a very narrow magnetite rim, which amounts to only 1/10 of the diameter, and the predominant core 9/10 **(Ac)** representing the most approximate chemical composition of original chromite or a very early stage of its alteration (Table 1). The ferrichromite intermediate zone was not recognized optically, but verified by beam-scan photographs (Plate IV).

Cation proportions are normalized to 3 and all spinels calculated on the basis of 4 oxygens for the ideal formula $A^{2+}B^{3+}O_4$ (Table 4). Total Fe was determined as FeO and it was partitioned as FeO and Fe_2O_3 assuming a balanced spinel with $RO/R_2O_3=1$. The composition of the core (mole %) is approximately as follows: 66.07 chromite, 16.91 hercynite, 12.57 gahnite, 3.49 galaxite, 0.57 magnetite, 0.22 vanadian spinel, 0.14 trevorite, and 0.03 ilmenite.

This is an aluminium chrome-spinel with anomalously high content of ZnO and MnO. The contents of Ti and Ni are very low, while the V content is moderate. The content of FeO is high, and that of Fe_2O_3 very low .

The high content of Zn in the Zagrlski Brook deposit is associated with very low MgO and Fe_2O_3, whereas the content of FeO is high. Very similar conclusions are stated by THAYER et al. (1964), SPRY &

Elements	Conc. in wt.%	RO R_2O_3	in wt.%	Cations	Error in %	LOD in ppm
Mg	n.d.	MgO	n.d.	-	-	954.2
Al	8.21555	Al_2O_3	15.52328	0.65551	1.0	426.2
Ti	0.01061	TiO_2	0.01770	0.00044	61.9	118.3
V	0.10530	V_2O_3	0.15491	0.00443	10.19	184.3
Cr	31.92894	Cr_2O_3	46.66415	1.32179	0.27	165.3
Mn	0.89087	MnO	1.14967	0.03490	10.51	2562.7
Fe_{tot}	22.51227	FeO	28.96204	0.86776	0.54	463.9
Fe^{2+}	22.04508	FeO	28.31600	0.84134	0.54	463.9
Fe^{3+}	0.46719	Fe_2O_3	0.66794	0.01783	0.54	463.9
Ni	0.03842	NiO	0.04889	0.00140	28.71	137.0
Zn	3.71521	ZnO	4.62469	0.12236	1.92	337.2
Σ	67.41717		97.21223	3.00000		
S	0.09800	FeS_2	0.18127			

Table 1. Microprobe analyses of the sample A.

Element	Core Bc	Fchr Bfc	Rim Br	RO R_2O_3	Core Bc	Fchr Bfc	Rim Br	Element	Cation Proportions Core Bc	Fchr Bfc	Rim Br
Mg	0.364	0.080	0.429	MgO	0.604	0.132	0.711	Mg	0.037	0.009	0.052
Al	3.201	0.395	0.327	Al_2O_3	6.063	0.747	0.617	Al	0.293	0.039	0.036
Ti	0.124	0.147	0.096	TiO_2	0.208	0.245	0.159	Ti	0.007	0.008	0.006
V	0.062	0.050	0.036	V_2O_3	0.091	0.073	0.053	V	0.003	0.003	0.002
Cr	23.422	15.574	2.525	Cr_2O_3	34.232	22.764	3.691	Cr	1.111	0.799	0.144
Mn	0.862	0.592	0.027	MnO	1.113	0.764	0.035	Mn	0.039	0.029	0.002
Fe_{tot}	38.662	55.255	69.026	FeO	49.739	71.085	88.802	Fe_{tot}	1.418	2.068	2.757
Fe^{2+}	22.680	24.505	23.659	FeO	29.177	31.526	30.438	Fe^{2+}	0.832	0.917	0.945
Fe^{3+}	15.982	30.750	45.366	Fe_2O_3	22.850	43.963	64.860	Fe^{3+}	0.586	1.151	1.812
Ni	0.056	0.103	0.121	NiO	0.072	0.130	0.154	Ni	0.002	0.005	0.001
Zn	2.390	0.994	0.010	ZnO	2.975	1.237	0.013	Zn	0.090	0.041	0.001
Σ	69.143	73.190	72.596		95.095	97.175	94.231		3.000	3.000	3.001
				$+Fe_2O_3$	2.289	4.403	6.496				
					97.289	101.578	100.730				

Table 2. Microprobe analyses of the sample B. Abbreviations are explained in the text.

Element	Core Cc	Rim Cr	RO R_2O_3	Core Cc	Rim Cr	Cations	Core Cc	Rim Cr
Mg	0.113	0.088	MgO	0.187	0.146	Mg^{2+}	0.014	0.011
Al	0.114	0.358	Al_2O_3	0.216	0.676	Al^{3+}	0.013	0.040
Ti	0.072	0.061	TiO_2	0.120	0.102	Ti^{4+}	0.005	0.004
V	0.099	0.024	V_2O_3	0.145	0.035	V^{3+}	0.006	0.001
Cr	0.289	0.082	Cr_2O_3	0.422	0.120	Cr^{3+}	0.017	0.005
Mn	0.024	0.000	MnO	0.030	-	Mn^{2+}	0.001	-
Fe_{tot}	70.700	71.822	FeO_{tot}	90.956	92.399	Fe^{2+}	2.938	2.934
Fe^{2+}	23.597	24.087	Fe^{2+}	30.312	30.988	Fe^{2+}	0.979	0.984
Fe^{3+}	47.103	47.735	Fe^{3+}	67.393	68.247	Fe^{3+}	1.959	1.950
Ni	0.081	0.097	NiO	0.103	0.124	Ni^{2+}	0.004	0.005
Zn	0.025	0.000	ZnO	0.031	-	Zn^{2+}	0.001	-
			Fe_2O_3	6.750	6.836			
Σ	71.55	72.533		98.959	100.439		3.000	3.000

Table 3. Microprobe analyses of the sample C.

A	**A core**	$(Fe^{2+}_{0.841}\ Zn_{0.122}\ Mn_{0.035}\ Ni_{0.001}\ Mg_{0.009})\ (Cr_{1.322}\ Al_{0.656}\ Fe^{3+}_{0.018}\ V_{0.004}\ Ti_{0.001})\ O_4$
B	**B core**	$(Fe^{2+}_{0.832}\ Zn_{0.090}\ Mn_{0.039}\ Ni_{0.002}\ Mg_{0.037})\ (Cr_{1.111}\ Al_{0.293}\ Fe^{3+}_{0.586}\ V_{0.003}\ Ti_{0.006})\ O_4$
	B fchr	$(Fe^{2+}_{0.917}\ Zn_{0.041}\ Mn_{0.029}\ Ni_{0.005}\ Mg_{0.009})\ (Cr_{0.799}\ Al_{0.039}\ Fe^{3+}_{1.151}\ V_{0.003}\ Ti_{0.008})\ O_4$
	B rim	$(Fe^{2+}_{0.945}\ Zn_{0.001}\ Mn_{0.002}\ Ni_{0.001}\ Mg_{0.052})\ (Cr_{0.144}\ Al_{0.036}\ Fe^{3+}_{1.812}\ V_{0.002}\ Ti_{0.006})\ O_4$
C	**C core**	$(Fe^{2+}_{0.979}\ Zn_{0.001}\ Mn_{0.001}\ Ni_{0.001}\ Mg_{0.014})\ (Cr_{0.017}\ Al_{0.013}\ Fe^{3+}_{1.959}\ V_{0.006}\ Ti_{0.001})\ O_4$
	C rim	$(Fe^{2+}_{0.984}\ Zn_{0.000}\ Mn_{0.000}\ Ni_{0.001}\ Mg_{0.011})\ (Cr_{0.005}\ Al_{0.040}\ Fe^{3+}_{1.950}\ V_{0.001}\ Ti_{0.004})\ O_4$

Table 4. Formulae of the mineral phases in the samples A, B and C.

SCOTT (1986), and by ZAKRZEWSKI (1989) for the Kuså deposit. Anomalous high contents of Zn and Mn in chrome-spinels (more than 0.5 wt % Zn and 0.3 wt % Mn) are a useful indicator of mineralized ultramafic sequences (GROVES et al., 1977). WYLIE et al. (1987) emphasize that chromite rich in Zn is considered unusual enough to be reported in the literature whenever it is found. These kind of zincian chromites are found in many deposits as reported by THAYER et al. (1964), WYLIE et al. (1987) and others.

2.2. MICROPROBE ANALYSES OF THE ZONED CHROME-SPINEL

The **sample B** represents a distinctly optically zoned chrome-spinel with four alteration zones: **Bc** (core), **Bfc** (two narrow intermediate ferrichromite zones), **Br** (magnetite rim). The results of the analyses are presented in Table 2 and formulae in Table 4.

The results of the three analyses and cation ratios (Tables 5 and 6) distinctly show the differences in the chemical composition from the core to the rim through two very narrow ferrichromite zones. The core is poorer in Al, Cr, Fe_{tot}, Zn, and V; much richer in Fe^{3+}, Ni and Ti and has approximately the same Mn content, when compared with the core **(Ac)** of the chrome-spinel grain **A** (Table 1).

This variation in chemical composition between these two cores indicates the character of the alteration processes of the original chromite in the Zagrlski potok deposit. The ferrichromite zone is strongly enriched in Fe_{tot} and Fe^{3+}, slightly in $Fe^{2+,}$ Ti and Ni, and distinctly poorer in Al, Mg and Zn, less so in Cr, Mn and V.

The outer magnetite zone (rim) shows additional very strong impoverishment in Cr, Mn and Zn, less in Ti and V, then strong enrichment in Fe^{3+}, Fe_{tot}, and slight enrichment in Ni and Mg. The content in Fe^{2+} remains the same.

The changes in the chemical composition from the core to the rim are very noticeable in the results shown in Table 4 and in Figs. 5-7.

2.3. OPTICALLY UNZONED MAGNETITE WITH CRYPTIC CHEMICAL ZONATION

In addition to occurring as rims on ferrichromite, or on cores, magnetite occurs as individual grains or aggregates dispersed throughout the host sulphides or gangue minerals.

Magnetite porphyroblasts can reach 1-3 mm in diameter. A magnetite grain (C) within the gangue material which consists of siderite, albite and rare quartz was selected for the microprobe analysis. This grain (0.54 x 0.34 mm) contained barely visible inclusions of the gangue minerals. Two microprobe analyses were made, firstly from the center of the grain (Cc), and secondly close to the margin (Cr) (Table 3). Two beam scan photographs (Plate VI) were taken to provide a general picture of the accumulation of chromium (a) and iron (b). The photograph (a) shows distinct chemical zonality of the optically unzoned grain. This is reflected by a slight enrichment of chromium in the core and the moderate enrichment in the zone near to the grain margin. In total, four different chemical zones can be distinguished.

The formulae are presented in Table 4, and cation ratios in Tables 5 and 6.

Table 3 shows that the optically unzoned magnetite grain shows cryptic chemical zonality. The the element wariations are expressed for Cr, Mn, Zn and V which are higher in the core, than in the outer zone. The amount of Fe_{tot}, Fe^{2+} and Fe^{3+} differ insignificantly, but

Samples	**Ac**		**Bc**		**Bfc**		**Br**		**Cc**		**Cr**	
Components		%		%		%		%		%		%
RCr_2O_4	1.982	66.07	1.666	55.53	1.199	39.97	0.216	7.20	0.051	1.70	0.007	0.23
RAl_2O_4	0.993	33.10	0.440	14.67	0.050	1.97	0.054	1.80	0.020	0.67	0.060	2.00
RFe_2O_4	0.017	0.57	0.876	29.20	1.724	57.46	2.715	90.50	2.910	97.00	2.923	97.43
RV_2O_4	0.007	0.23	0.005	0.17	0.002	0.07	0.003	0.10	0.009	0.30	0.002	0.07
$RTiO_3$	0.001	0.03	0.013	0.43	0.016	0.53	0.012	0.40	0.010	0.33	0.008	0.27
Σ	3.000	100	3.000	100	3.000	100	3.000	100	3.000	100	3.000	100

Table 5. Particular spinel components.

Samples	**Ac**	**Bc**	**Bfc**	**Br**	**Cc**	**Cr**
Cr/(Cr+Al)	0.669	0.791	0.953	0.801	0.568	0.106
Al/(Cr+Al+Fe^{3+})	0.329	0.147	0.020	0.018	0.007	0.020
Fe^{3+}/(Cr+Al+Fe^{3+})	0.009	0.294	0.579	0.910	0.985	0.977
Fe^{3+}/(Fe^{2+}+Fe^{3+})	0.024	0.413	0.557	0.657	0.667	0.664
Fe^{2+}/(Fe^{2+}+Fe^{3+})	0.979	0.587	0.444	0.343	0.333	0.335
(Mg+Zn)/(Mg+Zn+Fe^{2+})	0.127	0.133	0.051	0.052	0.016	0.011
Mg/(Mg+Fe^{2+})	<0.011	0.043	0.009	0.052	0.014	0.011
mg=100Mg/(Fe^{2+}+Mg+ +Mn+Zn+Ni	<1.000	3.700	0.900	5.200	1.400	1.100
Cr/Fe in weight percent	1.418	0.606	0.282	0.037	0.004	0.001
Co/Ni in weight percent	4.520	2.680	2.900	3.090	4.230	4.280

Table 6. Different reciprocal cation ratios.

Sample	**Zone**	**Cr**	**Fe^{2+}**	**Fe^{3+}**	**Al**	**Zn**	**Mn**	**Mg**	**Ti**	**V**	**Ni**	**Total**
A	**A core**	31.93	22.51	0.47	8.22	3.72	0.89	<0.10	0.01	0.11	0.04	67.42
B	**B core**	23.42	22.68	15.98	3.20	2.39	0.86	0.36	0.12	0.06	0.06	69.14
	B fchr	15.57	24.51	30.75	0.40	0.99	0.59	0.08	0.15	0.05	0.10	73.19
	B rim	2.53	23.66	45.37	0.33	0.01	0.03	0.43	0.10	0.04	0.12	72.60
C	**C core**	0.29	23.60	47.10	0.11	0.03	0.02	0.11	0.07	0.10	0.08	71.55
	C rim	0.08	24.09	47.74	0.36	0.00	0.00	0.09	0.06	0.02	0.10	72.53

Table 7. Proton microprobe analyses of zincian-chrome-spinel from the Busovača deposit, Bosnia.

Sample	**Zone**	**Cr_2O_3**	**FeO**	**Fe_2O_3**	**Al_2O_3**	**ZnO**	**MnO**	**MgO**	**TiO_2**	**V_2O_3**	**NiO**	**Total**
A	**A core**	46.66	28.32	0.67	15.52	4.62	1.15	<0.16	0.02	0.15	0.05	97.21
B	**B core**	34.23	29.18	22.85	6.06	2.98	1.11	0.60	0.21	0.09	0.07	97.29
	B fchr	22.76	31.53	43.96	0.75	1.24	0.76	0.13	0.25	0.07	0.13	101.58
	B rim	3.69	30.44	64.86	0.62	0.01	0.04	0.71	0.16	0.05	0.15	100.73
C	**C core**	0.42	30.31	67.39	0.22	0.03	0.03	0.19	0.22	0.12	0.10	98.96
	C rim	0.12	30.99	68.25	0.68	0.00	0.00	0.15	0.10	0.04	0.12	100.47

Table 8. RO and R_2O_3 components.

they are greater in the outer zone. The chemical zonality revealed on the beam-scan photographs (Plate VI) is more expressive.

2.4. INTERPRETATION OF THE MICROPROBE ANALYSES AND DIAGRAMS

Tables 7 and 8 present the values of the 10 elements and their RO and R_2O_3 components (in wt %) of all analysed samples. The diagrams (Figs. 3-7) highlight the behaviour of the zincian chrome-spinel during the early, intermediate and late stages of the alteration processes.

2.4.1. The Cr-Al-Fe^{3+} triangular classification (STEVENS, 1944)

In the above classification triangle the sample Ac plots in the field of zincian aluminium chromite, the core of the sample Bc in the field of zincian ferrian chromite, whereas the ferrichromite zone Bfc plots in the field of chromian magnetite near the border to the ferrian chromite field. The outer magnetite zone Br of the sample B and both zones of the sample C (Cc and Cr) plot at the corner marked with Fe^{3+}, i.e. the chromian magnetite field (Fig. 3). The alteration process passes through aluminian-chromite, ferrian chromite and chromian magnetite fields, ending at the corner marked by magnetite.

2.4.2. The alpine-stratiform field (THAYER, 1970)

The results of the analysis of the core from the sample Ac plot the zincian chrome-spinel in the stratiform field (Fig. 4). Taking into consideration that the analysis from the sample Ac already reflects an early stage of the alteration process, the position of unaltered material may have been in the alpine field (A_0 in Table 4).

2.4.3. Cation proportions in studied samples

Zincian chrome-spinel cores are extremely enriched in Cr_2O_3 and ZnO, rich in MnO, low in TiO_2, and very low in MgO (Figs. 5 and 6).

"Ferrichromite" zones are strongly enriched in

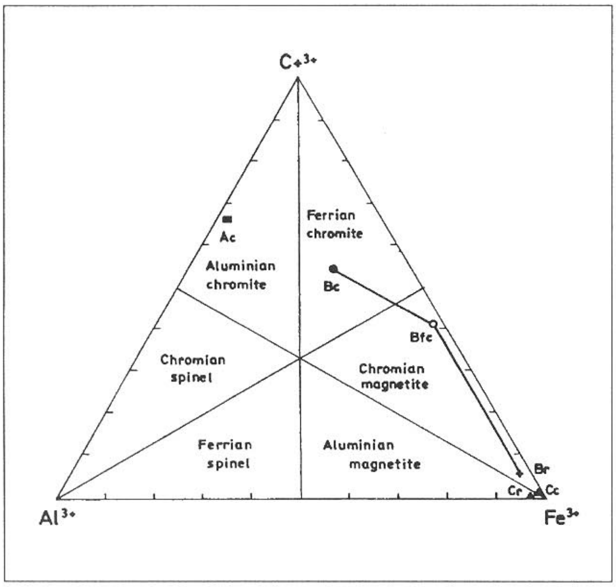

Fig. 3. Distribution of the studied chromites-ferrichromites in the Cr-Al-Fe^{3+} triangular classification of STEVENS (1944). For symbols Ac, Bc, Bfc, Br, Cc and Cr see text.

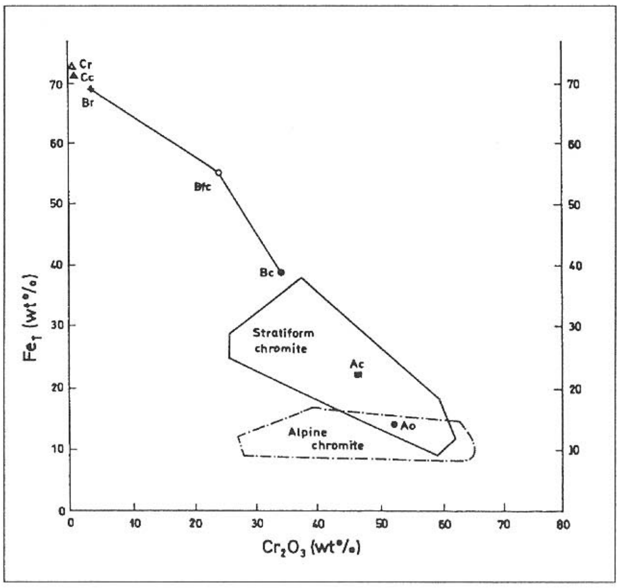

Fig. 4. Plot of the total iron (Fe_{tot} wt.%) vs. Cr_2O_3 (wt.%) for the studied chrome-spinels from Busovača. Fields for chromites from Alpine (dashed lines) and stratiform complexes (solid lines) are given after THAYER (1970).

Fe_2O_3, but distinctly poor in Al_2O_3, Cr_2O_3, MnO and ZnO.

Magnetite rims are characterized by exceptionally low ZnO, MnO, Al_2O_3; low Cr_2O_3, but very high Fe_2O_3 contents. The TiO_2, V_2O_3 and NiO content is either very slightly enriched (Ni) or depleted (V, Ti).

From the core to the rim the process of alteration is characterized by high constant enrichment in Fe_2O_3 (from 0.67 to 68.25 wt %), a slight increase or stagnancy in FeO (28.32 to 31.53 wt %), decrease in Al_2O_3, Cr_2O_3, MnO, ZnO; and slight enrichment or depletion in Ti, V, and Ni (Fig. 6).

2.4.4. Variation diagrams for the spinel compositions

(a) A general increase in the $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ and $Fe^{3+}/(Fe^{3+}+Al+Cr)$ ratios of spinels occurs within the sequence Ac, Bc, Bfc, Br, Cc, and Cr (Fig. 7).

(b) A general decrease occurs in: (1) the $(Zn+Mg)/(Zn+Mg+Fe^{2+})$ ratio (slight); (2) the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio (strong) and (3) the $Al/(Cr+Al+Fe^{3+})$ ratio in the same sequence, from Ac to Cc.

(c) A smooth increase in the Cr/(Cr+Al) ratios in the samples Ac, Bc and Bfc, but rapid decrease in the samples Br, Cc and Cr.

(d) A general similarity in all cation ratios concerning Bfc, Cc and Cr magnetite zones.

Figure 7 and Table 5 show results which indicate that (1) the alteration process developed under conditions of increasing f_{O2} in an open system (with respect to oxygen). This led to a progressive increase in the $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ and $Fe^{3+}/(Fe^{3+}+Al+Cr)$ ratios in the successive stages of the alteration process; (2) A more rapid diffusion of aluminium rather than chromium occurred during earlier stages of the alteration process from the core outward; (3) A general similarity in all cation ratios concerning Br, Cc and Cr suggesting a genetic relationship between optically unzoned magnetite grains and the different types of the magnetite rims in the optically zoned crystals.

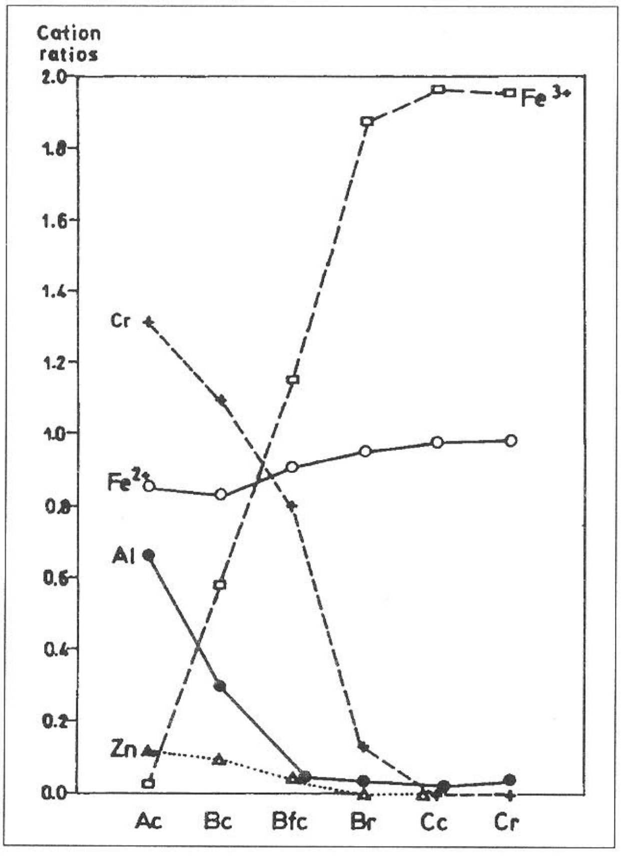

Fig. 5. Cation ratios of Zn, Al, Fe^{2+}, Cr and Fe^{3+} in studied samples A, B and C.

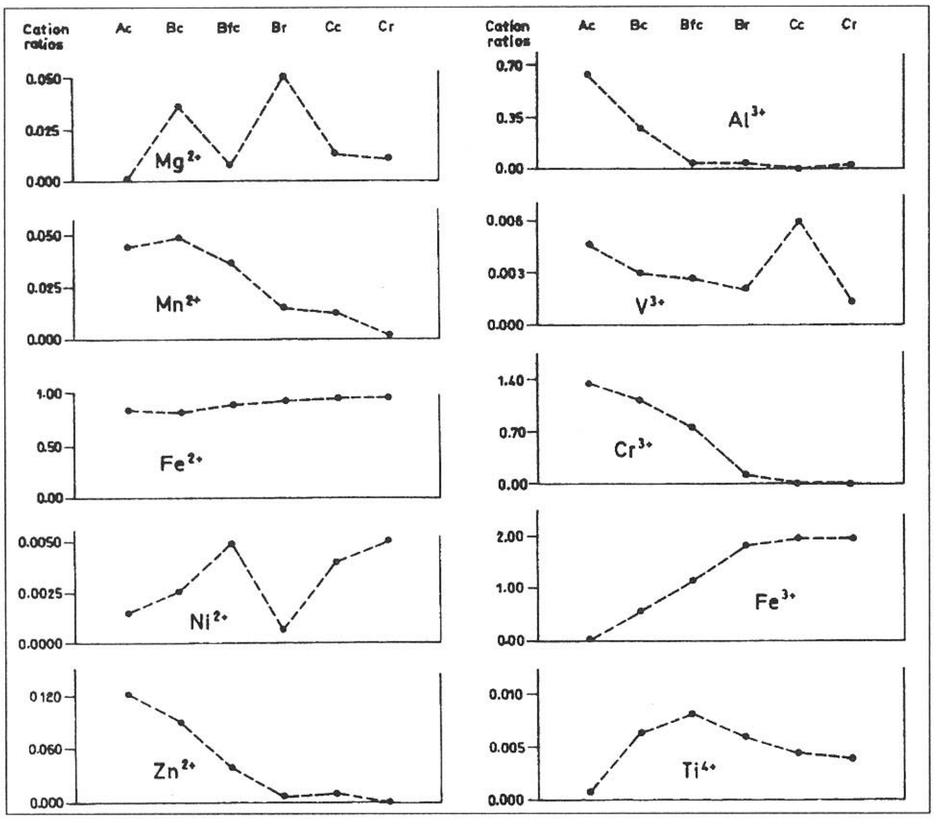

Fig. 6. Cation ratios of bivalent cations Mg^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Zn^{2+}, and of trivalent cations Al^{3+}, V^{3+}, Cr^{3+}, Fe^{3+} and Ti^{4}.

2.4.5. Beam-scan photographs

These photographs reveal more variable chemical compositions and more chemical zones than either observed optically or determined by microprobe analyses.

(a) A very narrow intermediate chromite zone occurs between the core and magnetite rim (Plate IV, Figs. 1, 2). This zone contains 16-20 wt % Cr and apparently more Fe than the core zone. The magnetite rim contains 8-16 wt % Cr and unevenly distributed Fe_{tot} (33-70 wt % Fe). Figures 3 and 4 (Plate IV) show the sharp difference in Al and Zn at the interface between the chrome-spinel core and the cryptically formed ferrichromite zone. The distribution of the Mn is more regular.

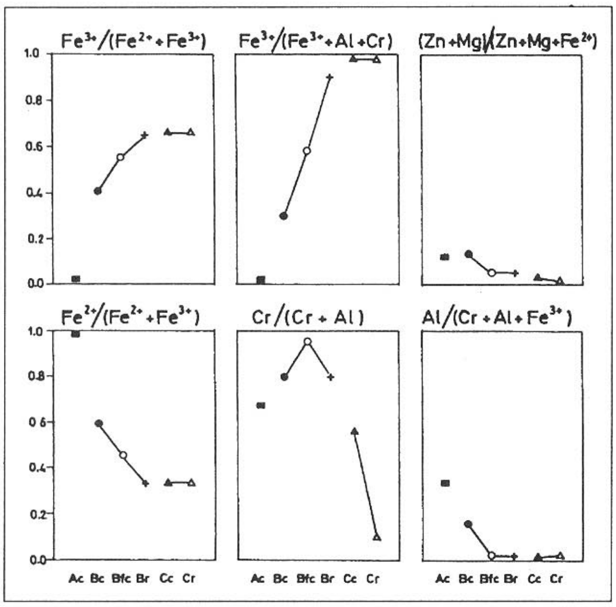

Fig. 7. Variation diagrams depicting spinel compositions in samples A, B and C (see Table 6).

(b) Plate V shows the distribution of all three optically observed zones (**Bcore, Bfchr, and Brim).** In the core, which is optically uniform, two distinct chemical zones can be distinguished on the beam-scan photographs. The analysis **Bcore** was made close to the interface of these two zones. The inner core zone is much richer in **Cr**, and poorer in Fe than suggested by analysis of the **Bcore** sample (Table 1). Al and Zn are mostly confined to this inner zone.

(c) Beam-scan photographs (Plate VI) of **sample C** distinctly show the chemical zonality of the optically unzoned magnetite grain. The slight enrichment of chromium in the core and much stronger enrichment in the zone near to the outer border can be recognized. In total four different chemical zones can be differentiated. The outer chromium rich zone is probably the result of the low-grade regional progressive Alpine metamorphism.

3. GENETIC REMARKS

3.1. SOURCE OF ZINC AND TIME OF ITS INTRODUCTION

The association between zincian spinel and metamorphosed sulphide deposits has been reported by THAYER et al. (1964), GROVES et al. (1977), SPRY

& SCOTT (1986), WYLIE et al. (1987), MOGESSI et al. (1988), and ZAKRZEWSKI (1989).

The fact that zincian chrome-spinel (sample Ac) from the Busovača deposit was hardly affected by the alteration process, forming an exceptionally narrow magnetite rim (only 1/10 of the diameter) and a cryptically formed ferrichromite zone, proves that the introduction of the zinc was prior to the alteration process during a reduction phase, in the closed system, with very low f_{O2}, most probably synchronous with the Fe-Cu-Co-Ni-Zn sulphide mineralization. Such an opinion is supported by the fact that the high Zn content of the analysed chrome-spinel core (Ac) in sulphide ores relative to the sulphide fraction itself (which is poor in Zn), confirms strong partition of Zn to the oxide phase as suggested by MacLEAN & SHIMAZAKI (1976) and SHIMAZAKI & MacLEAN (1976). We found an inverse correlation between ZnO and MgO in the spinel core (Ac). This core is anomalously low in MgO (less than 0.15 wt %) indicating that as ZnO was added to the chrome-spinel MgO was removed. The same fact was reported by THAYER et al. (1964) and WYLIE et al. (1987).

The sulphur isotope data obtained from pyrite in the vertical profile of the Busovača deposit varies from +0.29 ‰ for $\delta^{34}S$ (upper profile) to +0.43 ‰ for $\delta^{34}S$ (the lower and middle profile) (JURKOVIĆ et al., 1992), is compatible with the idea that it might have been derived from original magmatic sulphides. This has also been reported by MOGESSI et al. (1988) for the Oetzal-Stubai Complex (Austria).

The original chrome-spinel of the Busovača deposit, composed mainly of chromite, spinel and hercynite, equilibrated after the emplacement of the magma under high redox potential (f_{O2}). It was then exposed to the high temperature hydrothermal fluids, bearing mainly Fe^{2+}, Zn, Mn, S, of magmatic origin. The rock and segregated chromitites interacted with this fluid under a very low redox potential (as indicated by the presence of sulphides). Magnesium in chromite grains was almost completely replaced by Zn, Mn and Fe^{2+}. Pyrite, chalcopyrite, subordinate amounts of siegenite, enargite and bornite were formed simultaneously. This disequilibrium hydrothermal process caused strong metasomatism of chrome-spinel. WYLIE et. al. (1987) reported that the zinc metasomatism took place after chromite was incorporated in their host-rocks.

The problem of the genesis of the sulphides remains open because the very fine banding of sulphides and chrome-spinels in the Busovača deposit suggests a synchronous magmatic origin of this deposit. Such statements have been reported by CZAMANSKE et al. (1976) and ECONOMOU & NALDRETT (1984).

3.2. ALTERATION PROCESS AND FORMATION OF FERRICHROMITE

MICHAILIDIS (1990) summarized the different opinions of ferrichromite formation: (a) magmatic alteration; (b) pre-serpentinization origin; (c) serpentinization; (d) subsequent to serpentinization; (d) metamorphism. He described two types of alteration: (a) an epitaxial growth, and (b) a gradual transformation of chromite to ferrichromite and magnetite.

According to BEESON & JACKSON (1969) the alteration is a volume-for-volume replacement of MgO and Al_2O_3 by FeO and Fe_2O_3. The presence of a chromite core, ferrichromite and magnetite in close juxtaposition, is proof according to ULMER (1974) that the alteration occurred at temperatures at which solid solution between these phases could take place only very slowly, if at all. He interpreted the alteration as hydrothermal attack of the primary chromite to produce diffusion controlled chromite zoning.

WYLIE et al. (1987) and CANDELA et al. (1989) state that ferrichromite is not a reaction zone that forms between chromite and magnetite, rather it is most likely formed as a precipitate that is in local equilibrium with a solution that is deriving nutrient from an irreversibily dissolving chromite core.

BLISS & MacLEAN (1975) state that serpentinization cannot singularly form ferrichromite. This process does produce rims of secondary magnetite around chromite, and this "opens the possibility that ferrichromite may be formed by regional metamorphism of these rimmed grains". Metamorphism to at least epidote-amphibolite facies produced antigorite from lizardite, while the magnetite rims reacted with the chromite cores to produce Al- and Mg-poor ferrichromite zones.

On the basis of theoretical constructed isobar surfaces for f_{O2} within the spinel compositional prism IRVINE (1965) proved that the composition of the chromite core formed at a lower f_{O2} than the ferrichromite, whereas the composition of the magnetite rim also plots off the ferrichromite isobar surface, implying that it also formed under different conditions.

The alteration process of zincian chrome-spinel from Busovača took place in two phases: **(a) the early stage** with the preservation of the euhedral crystal outlines (volume-for-volume replacement) and formation of the ferrichromite and magnetite zones; **(b) the late stage**, characterized by decolourization of the cores (distortion of the lattice), by resorption or irregular dissolution of the cores ("atoll structure"), irregular patches and minute specks as the last relics of chrome-spinel inside magnetite grains. The alteration process began very early, but later than Zn-metasomatism (Plates II and III).

During the Hercynian and Alpine regional metamorphism the Busovača deposit and its ultramafic host and other adjacent rocks underwent greenschist facies metamorphism. This is supported by evidence as follows: formation of porphyroblasts (pyrite, albite, hyalophane); myrmekitic (interpenetrating) intergrowths of magnetite and gangue minerals, albite and hyalophane; recrystallization of plastic and softer minerals as chalcopyrite, enargite, bornite; siderite forming cement or filling interstices of harder minerals. The alkaline metasomatism (sodium, barium, silica-bearing, mobile fluids) formed tiny layers and nests of neoquartz, neoalbite, neosiderite, manganoan ankerite, chromian chlorite, phengitic muscovite and hyalophane. These neominerals have been identified by X-ray powder diffraction, microscopical analyses in polarized light, and chemical analyses (JURKOVIĆ et al., 1992).

3.3. MOBILITY AND MIGRATION OF Cr, Al, Mn

Chemical zoning in chrome-spinels from the Busovača deposit which took place during alteration gave rise to the release of Al, Cr, Zn and Mn from the crystal lattice. Such Al and Cr were taken up by the silicates, and reacting with them formed chromian-chlorite surrounding altered chromite grains; released Mn was taken up by neoankerite forming manganoan ankerite in the "pressure shadows" of the microfolds and microflexures, especially in the middle part of the vertical ore profile. Released chromium was included into chromian chlorite, siderite (PIXE gave even 0.72 wt % in the core) and pyrite porphyroblast (0.09 wt % Cr_2O_3 in core). These phenomena indicate the distinct mobility of Al, Cr, Mn, Zn away from chrome-spinel bearing magnetite within a distance of about at least a few hundred micrometres.

BEESON & JACKSON (1969) stated that the formation of chlorite is genetically related to the chromite alteration. MITRA (1972) supposed that the result of chemical zoning in chromites was the increase of trivalent iron in the spinel lattice, which became disordered, and thus Al was released from the crystal lattice, reacting with the serpentinous materials forming chlorite surrounding altered chromite grains. ONYEAGOCHA (1974) considered that the chromite alteration takes place above the upper stability limit of serpentine and below that of chlorite. SHEN et al. (1988) state that the outward diffusion of Mg and Al and the origin of chlorite and serpentine are related to the generation of interleaved layers of trioctahedral chlorite and serpentine in the matrix.

A solid state diffusion, i.e. the volume-for-volume replacement of chrome-spinel by ferrichromite, took place during an extended period of regional metamorphism. Retention of smooth euhedral grain shapes during the early stage of alteration suggests a type of epitaxial growth of the magnetite rims, which reacting with the chrome-spinel core produced transitive ferrichromite zones.

Afterwards, during the retrograde metamorphism, the additional decomposition described above occured during late stage alteration of chromite.

3.4. DIFFUSION RATES OF ELEMENTS DURING THE ALTERATION PROCESS

The diffusion rates of Al, Zn, Cr and Mn during the early, intermediate and late stages of alteration from the core outwards are presented in Table 9. The sequence ordered by decreasing rates is as follows: Al → Zn → Cr → Mn.

Microprobe analyses confirm the statement recorded from the step-scan analysis made by BEESON & JACKSON (1969) that replacement of Mg by Fe^{2+} in the spinel lattice preceeds that of Al by Fe^{3+}, and that FeO and Fe_2O_3 increase as MgO and Al_2O_3 decrease. The $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ ratio is fixed in turn as a result of P_{02} during alteration.

ULMER (1974) using EMA showed that the decrease in Al from chromite to ferrichromite occurs abruptly and completely at their interface, and thus a secondary inter-diffusion across a magnetite-chromite interface is not a possible explanation for ferrichromite formation. Our beam-scan photographs (Plates IV, V and VI) do not support such a statement. BLISS & MacLEAN (1975) consider that FeO, Fe_2O_3, NiO and TiO_2 diffuse inwards and replace Al_2O_3, MgO and Cr_2O_3 which diffuse outwards.

3.5. ALTERATION DIFFERENCES BETWEEN "ACCESSORY" AND "SEGREGATED" MAGNETITE

The upper part of the vertical profile in the Busovača deposit is characterized by magnetite porphyroblasts or small (very often automorphic) magnetite aggregates, optically unzoned, with the normal optical properties of magnetite.

The densely packed stringers or streaks (1 to 5 mm thick) consisting mostly of magnetite grains, especially in the lower and middle parts of the ore profile, comprise a significant number of optically zoned chrome-spinel cores. We share the opinions of IRVINE (1967) and LIPIN (1984) that the chromite in densily packed chromite layers ("the segregated" chromite) is less likely to be altered hydrothermally or re-equilibrated with adjoning silicates than scattered accessory grains. The densely packed chromite has a very small amount of other solid phases with which to react. ULMER (1974) reported McKAGUE's (1964) statement that the rimming of any kind is more thinly developed in "schlieren" than on disseminated chromite grains.

The beam-scan photographs (Plate VI) of the optically unzoned magnetite porphyroblast revealed its chemical zonality as shown by four cryptical, but different zones of chemical composition. The microprobe

	Al	Zn	Cr	Mn
(1) Between A core and B core	2.43	1.46	1.29	1.00
(2) Between A core and B fchr	5.50	1.67	1.04	1.00
(3) Between B core and B fchr	13.50	2.50	1.35	1.00

Table 9. Diffusion rates among Al, Zn, Cr, and Mn during early and late stages of alteration from the core outward (Busovača deposit). (1) early stage; (2) intermediate stage; (3) late stage.

analyses of the samples Cc and Cr show a great similarity to sample Br. All these facts suggest a mutual genetic relationship, i.e. an identical origin.

3.6. METAMORPHISM

The mineral assemblage of the Busovača deposit, consisting mainly of Al-poor chromian magnetite and subordinate ferrichromite, chrome-spinel relics and chromian chlorite, co-exists with the neighbouring para- and ortho-metamorphic complex belonging to the greenschist facies or to the transitive lower epidote-amphibolite facies.

The Busovača deposit mineral assemblage is consistent with the mineral assemblage of the surrounding metamorphic complex as defined by MAJER et al. (1991). Therefore metamorphism was the most important factor controlling transformations in the ore paragenesis.

The following opinions are emphasised concerning the role of the metamorphism in the composition of the chrome-spinels: THAYER (1966) and EVANS & FROST (1975) consider that progressive or retrograde metamorphism cause systematic changes in the chrome-spinel composition. The stable spinels in greenschist facies are Al-poor magnetite, chromian magnetite or ferrichromite, depending on the local Cr/Fe^{3+} ratio in the rock. With increasing metamorphic grade (up to middle amphibolite facies) spinels more enriched in Cr are encountered, containing moderate amounts of Al (as is the case of the Busovača deposit). MITRA (1972) stated that the zoning of the chromite was brought about by transformation of Fe^{2+} into Fe^{3+} at an early stage of metamorphism, activated by the in situ rock fluids. KIMBALL (1991) considers that the chrome-spinel compositions of metamorphic rocks change with metamorphic grade, manifested by an increase in the Cr/(Cr+Al) and/or $Fe^{2+}/(Fe^{2+}+Mg^{2+})$ ratios.

4. CONCLUSIONS

1) The tectonic setting, banded structure and mineral paragenesis characterized by the euhedral crystal outlines of chrome-spinel suggest a primary magmatic origin.

2) The incorporation of Zn was prior to the alteration process, during a reduction phase, in the closed system, with very low f_{O2}, most probably synchronous with the Fe-Cu-Co-Ni-Zn sulphide mineralization. The high Zn content of the analysed core of chrome-spinel, relative to the sulphide fraction itself, confirms strong partition of Zn to the oxide phase. The chrome-spinel shows the negative correlation between ZnO and MgO indicating the simultaneous addition of ZnO and removal of MgO. The core is characterized by an extremely low content of Fe_2O_3 component.

3) The chemical zonation of chrome-spinel caused by alteration gave rise to the increase in trivalent iron in the lattice of the spinels which were distorted and Al, Cr, Mn were released from the crystal lattice. The released Al was taken up by the silicates, and thus originated chlorite, which embraces altered chromite grains; the released Mn was taken up by neoankerite forming manganoan ankerite; and released Cr was included into chlorite, siderite and pyrite.

4) The diffusion rates among Al, Zn, Cr and Mn during early, medium and late stages of the alteration, decrease in the order of: Al → Zn → Cr → Mn. The replacement of Mg by Fe^{2+} in the spinel lattice preceeds that of Al by Fe^{3+}, FeO and Fe_2O_3 increase as MgO, ZnO and Al_2O_3 decrease.

5) The alteration process of zincian chrome-spinel took place in two phases: (a) the early stage with the preservation of the euhedral crystal outlines (volume-for-volume replacement) and formation of ferrichromite and magnetite zones; (b) the late stage, characterized by decolourization of the cores (distortion of the lattice), by resorption or irregular dissolution of the cores ("atoll structure"), irregular patches and minute specks as the last relics of chrome-spinel inside magnetite grains. The alteration process began very early, but later than Zn-metasomatism, and was completed during the Alpine regional metamorphism.

6) Textural features of the successive alteration phases of zincian chrome-spinel as well as the beam-scan photographs of the altered chrome-spinels indicate that the optically unzoned magnetite grains and aggregates originated in chrome-spinel.

7) The mineral assemblage of the Busovača deposit, consisting mostly of Al-poor chromian magnetite, and subordinate ferrichromite, chrome-spinel relics and chromian chlorite co-existing with the neighbouring para and ortho-metamorphic complex originated under P-T conditions of the greenschist facies.

Acknowledgements

Assistance was provided by the Institute "Rudjer Bošković", Zagreb, with the use of their PIXE facilities, and is gratefully acknowledged. Acknowledgement is made to the Ministry for Science and Technology for financial support. We would also like to thank Dr J. PAMIĆ for his critical reading of the manuscript.

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Manuscript received September 9, 1993.
Revised manuscript accepted May 23, 1994.

PLATE I
Figs. 1-4.

Typical structures and textures in the Busovača ore deposit visible on the polished sections. Magnetite (black) and pyrite (dark-grey) alternate with gangue minerals (white).

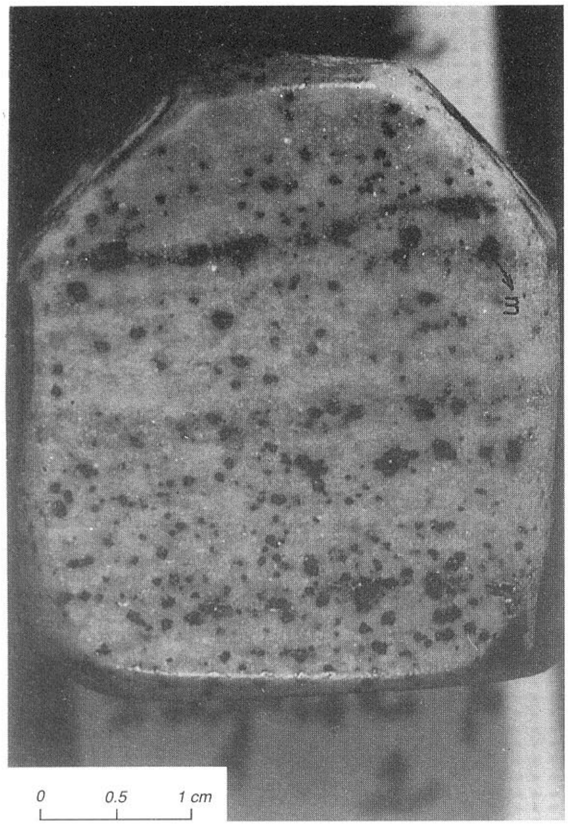
PLATE II
Figs. 1-6.

Polished section showing early stage alteration of the zincian chrome-spinels, Busovača deposit, Bosnia and Herzegovina.
Legend: **chr** chrome-spinel core, **fchr** ferrichromite intermediate zone, **mt** magnetite rim, **py** pyrite. Gangue minerals (black or dark grey areas) are siderite, albite, quartz, hyalophane, manganoan ankerite.

PLATE III
Figs. 1-6.

Polished section showing the late stage alteration of the zincian chrome-spinels, Busovača deposit, Bosnia and Herzegovina.
Legend: **chr** lobed or ragged relics of zincian chrome-spinel, **fchr** ferrichromite, **mt** magnetite, **py** pyrite, gangue black or dark gray areas. Figs. 3, 4 and 5 show almost myrmekitically intergrown of magnetite with gangue. The magnetite porphyroblasts on the Fig. 6 are cryptically zoned.

PLATE I



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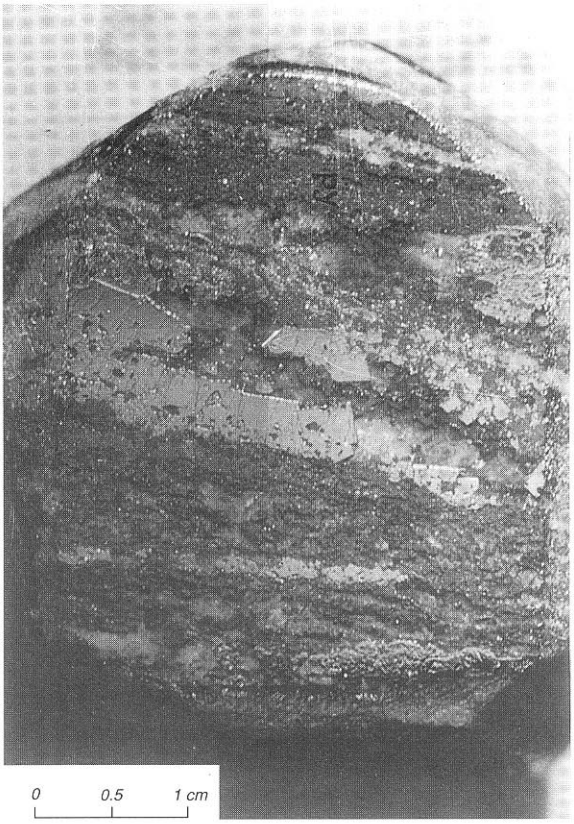

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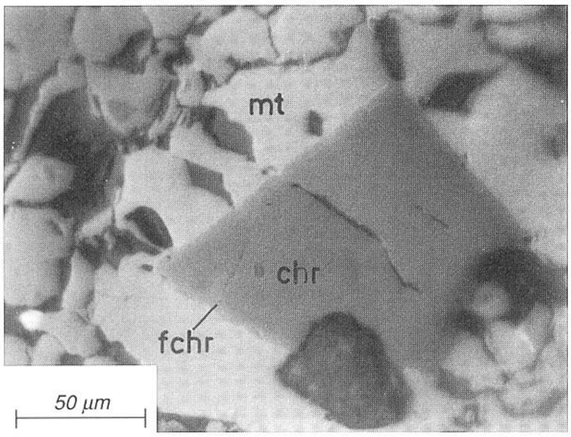
3

4

PLATE II



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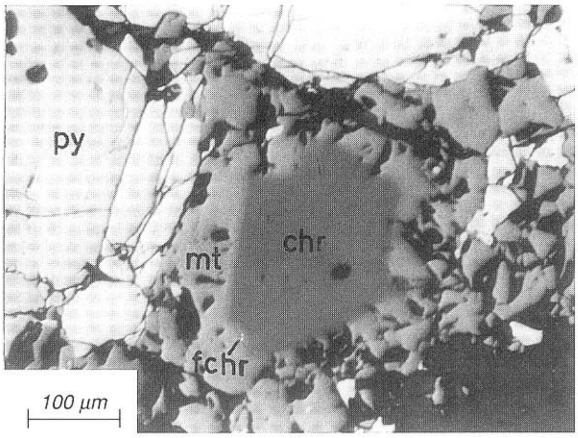

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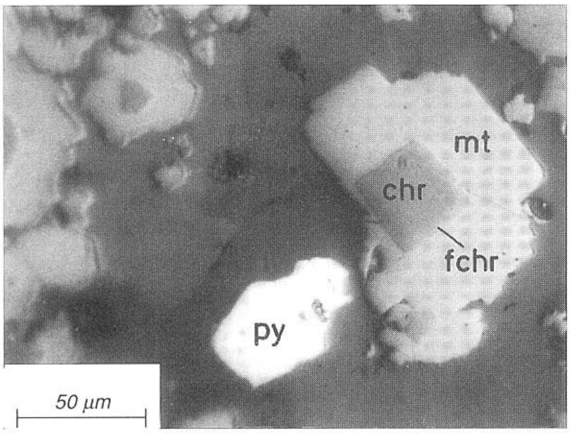

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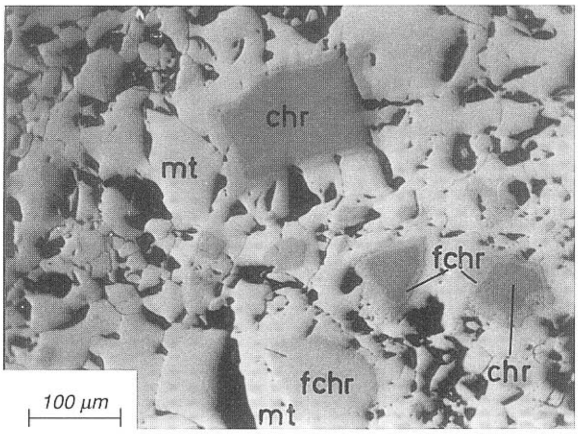

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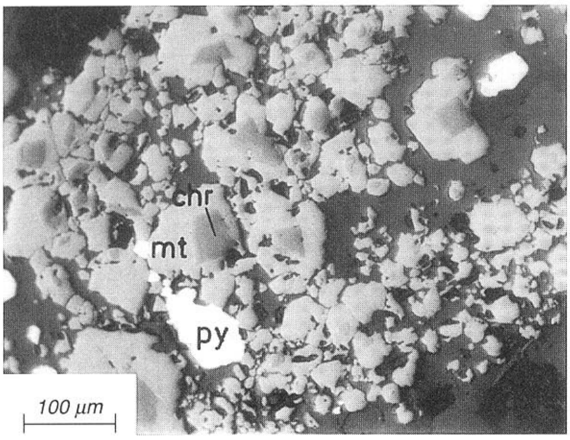

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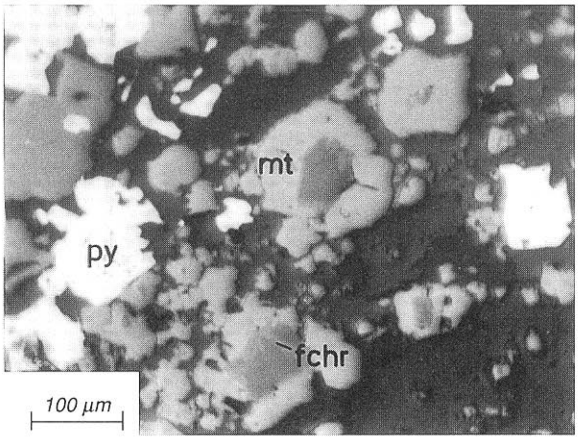

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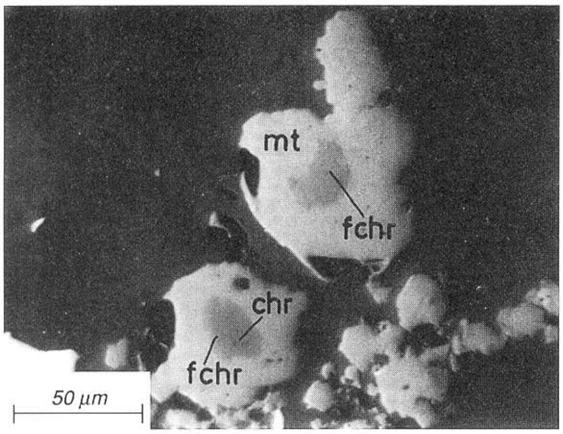
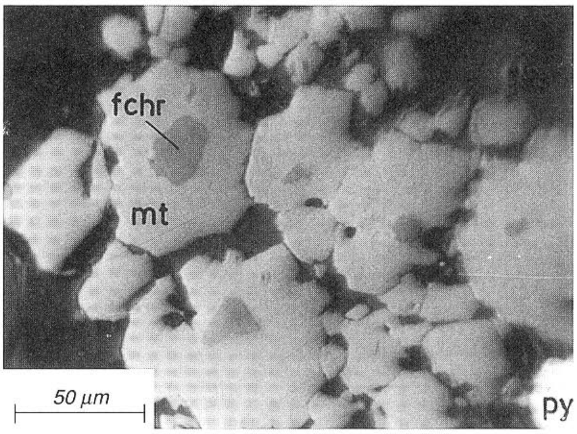

mt
fchr
chr
fchr
50 µm

1


fchr
mt
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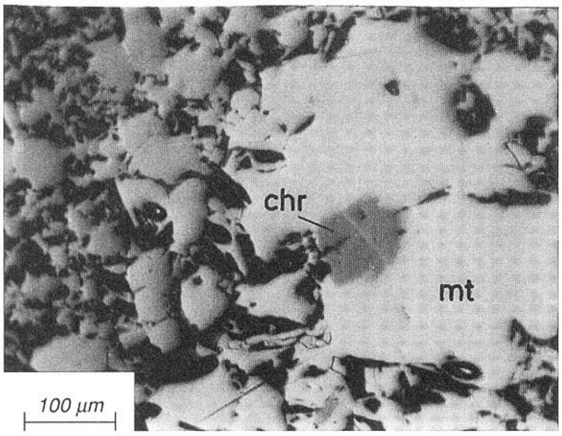
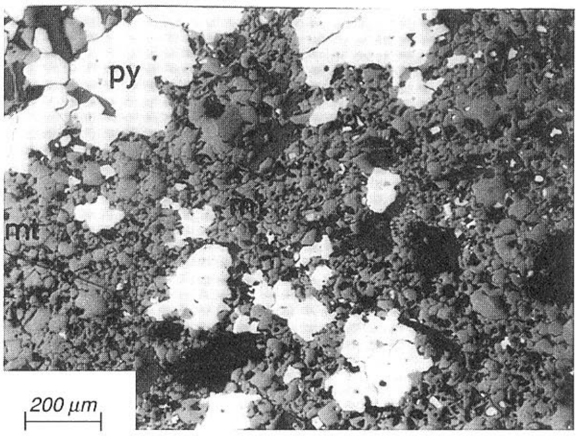
py

2


chr
mt
100 µm

3


py
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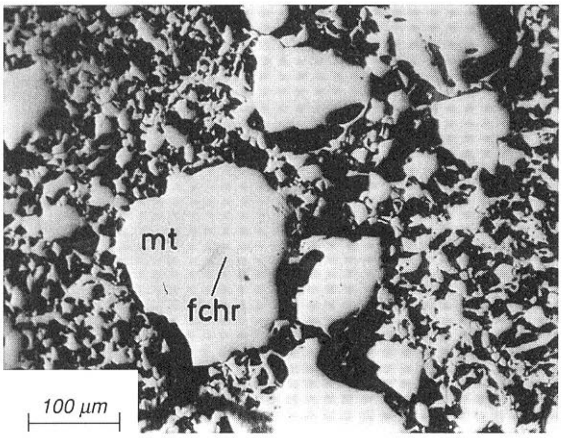
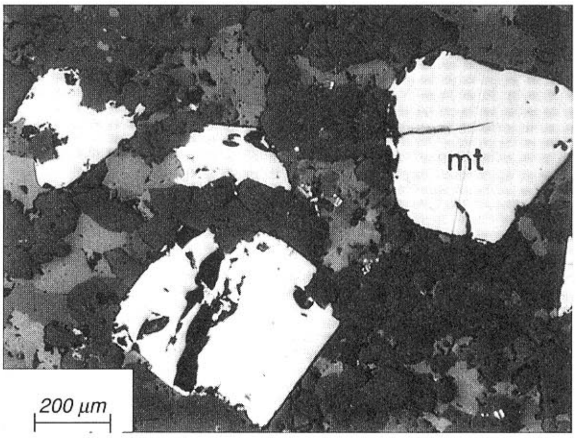

mt
fchr
100 µm

5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6

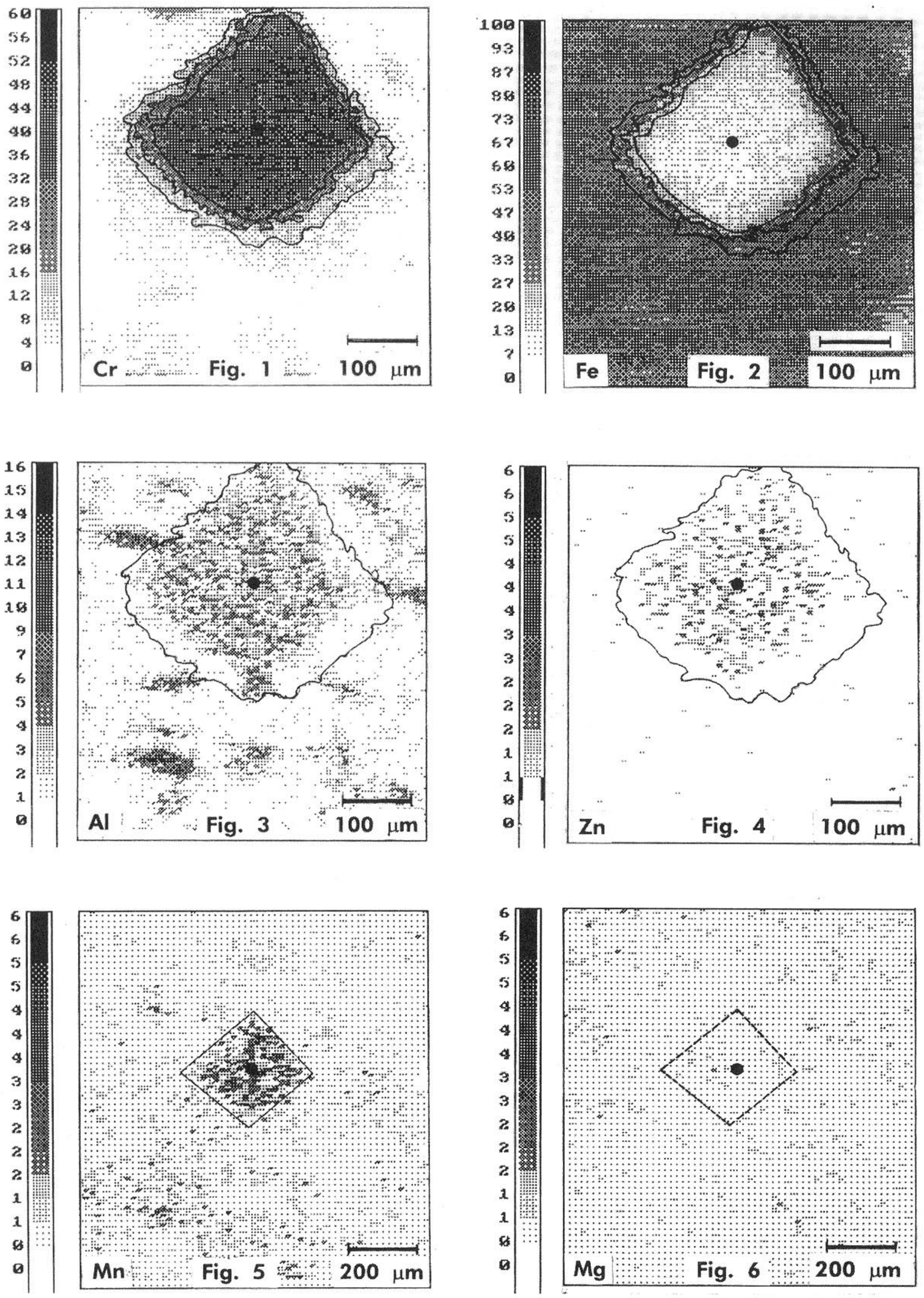

Plate IV

Beam scan photographs for Cr (Fig. 1), Fe (Fig. 2), Al (Fig. 3), Zn (Fig. 4), Mn (Fig. 5) and Mg (Fig. 6) in the sample A - euhedral grain of the zincian chrome-spinel with very narrow magnetite rim.
• - Position of the microprobe analysis (PIXE).
Busovača deposit, Bosnia and Herzegovina.

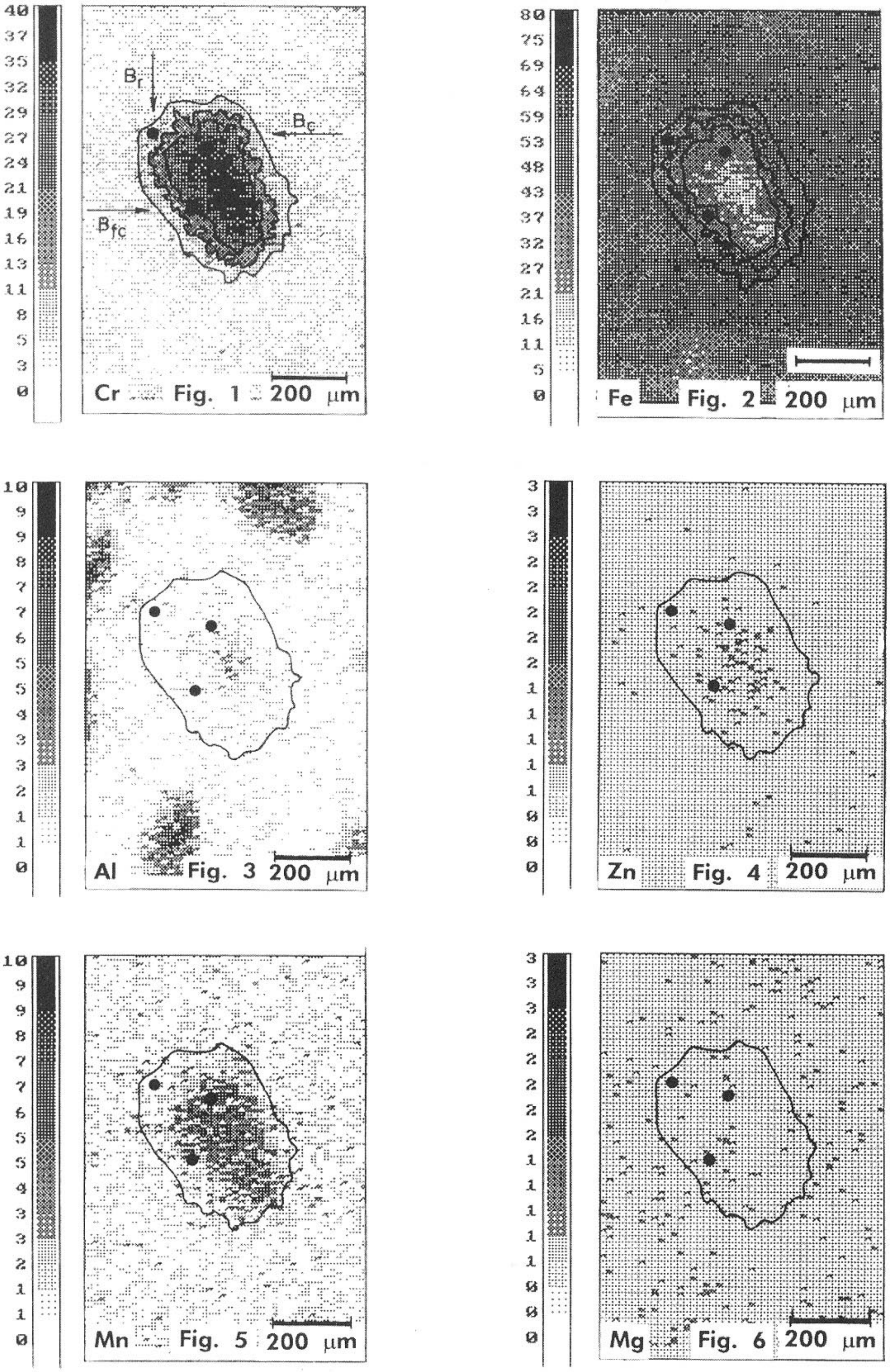

Plate V

Beam scan photographs for Cr (Fig. 1), Fe (Fig. 2), Al (Fig. 3), Zn (Fig. 4), Mn (Fig. 5) and Mg (Fig. 6) in the sample B - zoned zincian chrome-spinel, with core (B_c), ferrichromite intermediate zone (B_{fchr}) and outer magnetite rim (B_r) during the early alteration stage.

• - Positions of the three microprobe analyses (PIXE): B_c-core, B_{fc}-ferrichromite zones, B_r-magnetite rim.

Busovača deposit, Bosnia and Herzegovina.

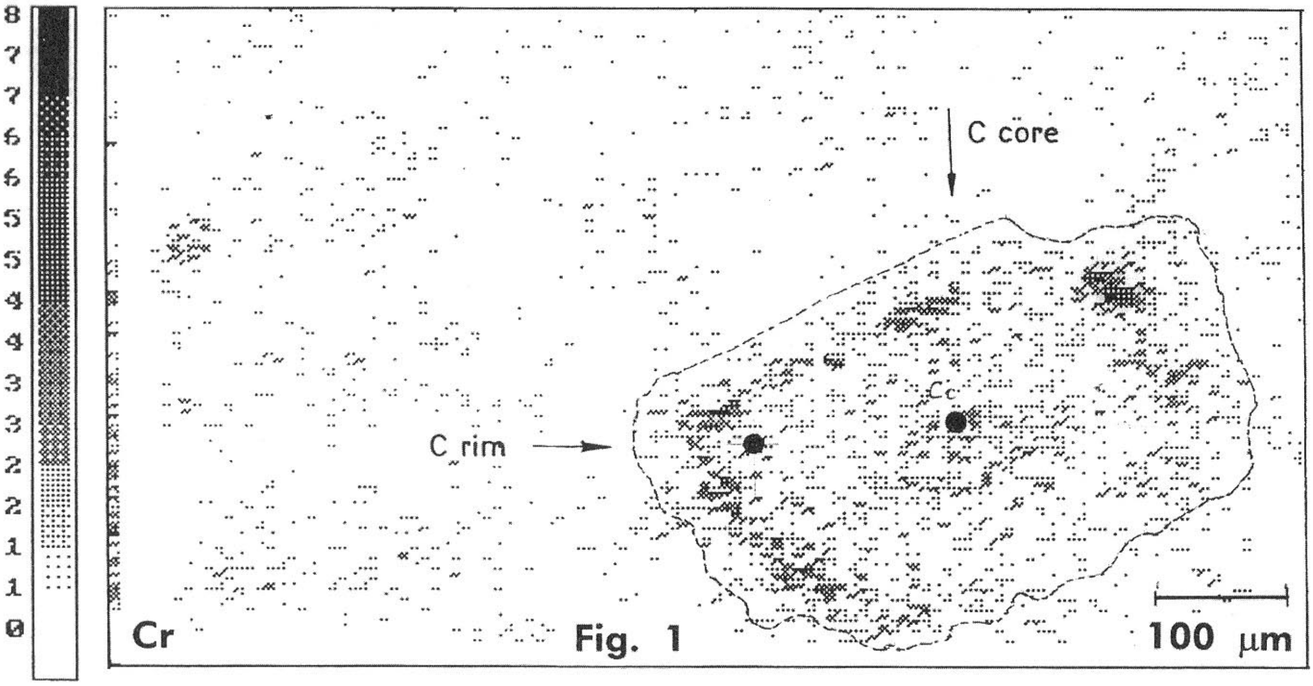

Fig. 1

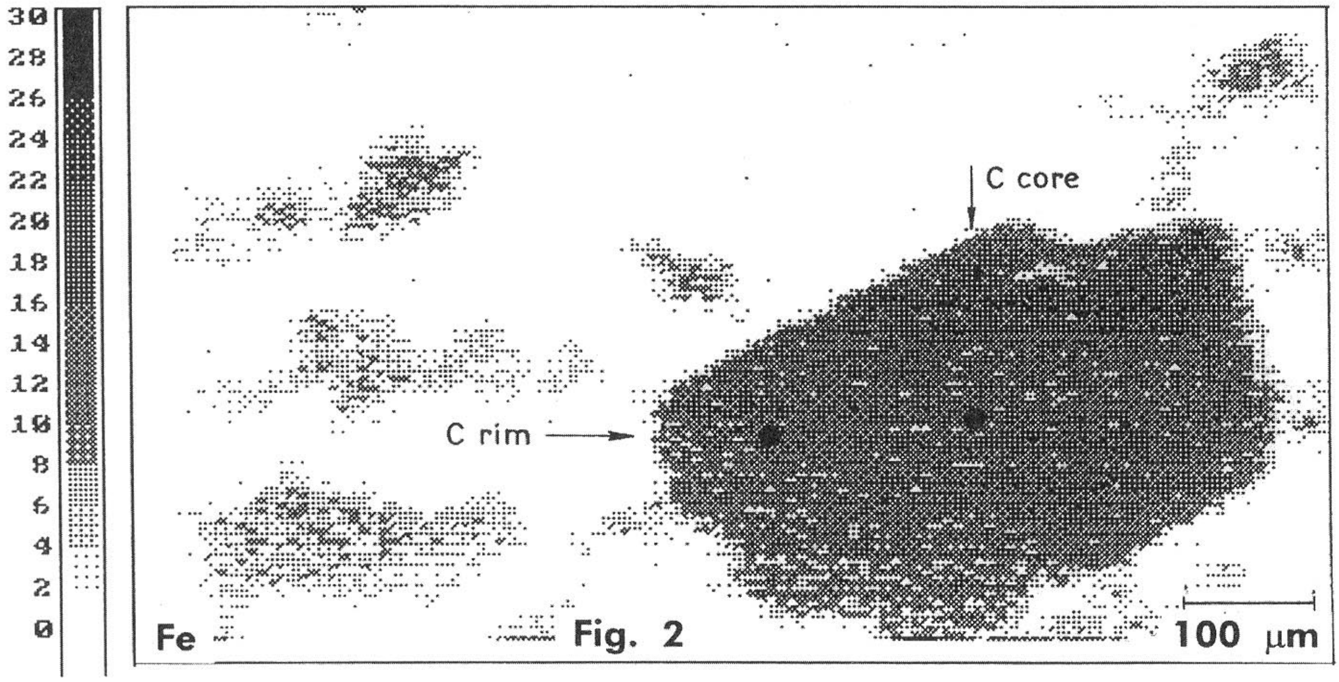

Fig. 2

Plate VI

Beam scan photographs for. Cr(Fig.1), and Fe(Fig.2) in the sample C - cryptically zoned magnetite porphyroblast, during the late stage alteration.

• - Positions of the two analyses - C core and C rim.

Busovača deposit, Bosnia and Herzegovina.